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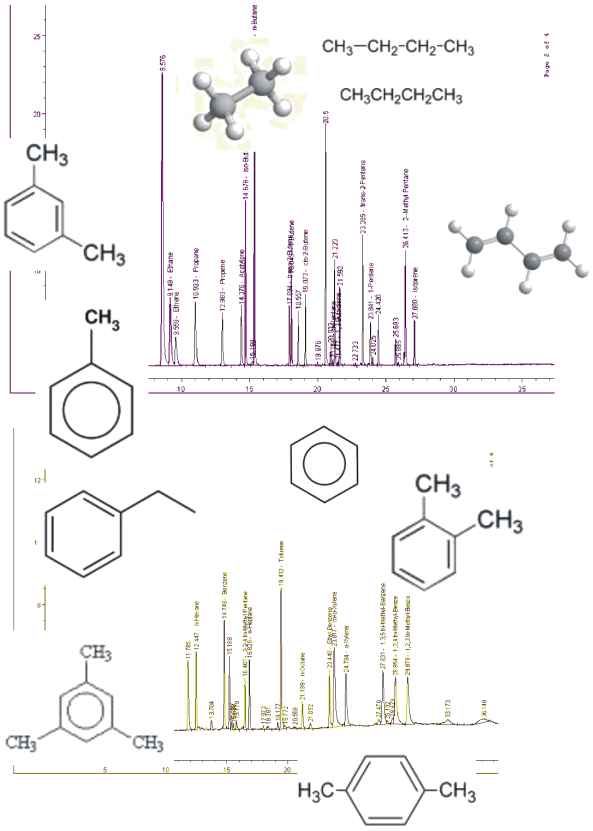
EC Intercomparison of VOC measurements between National Reference Laboratories (AQUILA network)



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Executive Summary

Between May 2007 and February 2008, cylinders from two mixtures (synthetic and ambient air) circulated amongst 18 AQUILA laboratories to evaluate their performance in the analysis of the 30 volatile organic compounds listed in the directive EC/50/2008.

The concentration for the compared mixtures was of circa 5 and 1 ppb per compound in the synthetic and ambient air mixture, respectively. Laboratories were asked to carry out five independent measurements for each mixture and provide values and associated uncertainties. A full description of the analytical method used by each laboratory and their calculations for the estimation of the uncertainties was also included in the report.

The results were finally expressed in terms of bias with respect to the reference value and the E_n number of the measurement. In general, analytical uncertainties were higher for the lower concentration mixture in comparison to the higher one. For the synthetic mixture, half of the laboratories reported a relative overall expanded uncertainties better than 10 %, whilst for the ambient air mixture, the same percentage of laboratories showed only values better than 20 %.

The heaviest hydrocarbons (123, 124 and 135 trimethyl benzene, m,p- xylene, ethyl-benzene and benzene) and those more reactive and lighter (like 1,3 butadiene, isoprene, 1-pentene) were analysed with more difficulty in comparison to the rest of the compounds.

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Nomenclature and Abbreviations

AEAT	AEA Technology
AOL-UUW	Amt der oberösterreichischen Landesregierung. Abteilung Umweltschutz / Labor
AQUILA	National Air Quality Reference Laboratories
B	benzene
Bias	$(C_{lab}-C_{ref})/C_{ref} \cdot 100$
CHMI	Czech Hydrometeorological Institute
C_i	the "i" concentration provided by a participant
$\overline{C_{lab}}$	average value of the 5 measurements of the cylinder
C_{ref}	concentration of the reference value
EARS	Environmental Agency of the Republic of Slovenia
EC	European Commission / European Committee
EMD	National Reference Laboratory (NRL)/LCSQA. Ecole des Mines de Douai
EMPA	Empa- Materials Science & Technology. Air Pollution/ Environmental Technology
E_n	$= \frac{C_{lab} - C_{ref}}{\sqrt{U_{lab}^2 + U_{ref}^2}}$
EPA	Environmental Protection Agency
ERLAP	European Reference Laboratory of Air Pollution
EUROMET	European Collaboration in Measurement Standards
FMI	Finnish Meteorological Institute
IDA	Laboratorio Referencia do Ambiente
ISCIII	Instituto de Salud Carlos III
ISO	International Standard Organization
ISP	isoprene
ISSeP	Institut Scientifique de Service Public
IVL	Swedish Environmental Research Institute
JRC	Joint Research Centre
mpX	m,p-xylene
n	number of individual measurements of the cylinder
NERI	Danmarks Miljøundersøgelser. National Environmental Research Institute
NPL	National Physical Laboratory
OEU	relative overall expanded uncertainty, %= $\left(U_{lab} + \left\| \overline{C_{lab}} - C_{ref} \right\|\right) / \overline{C_{lab}} \cdot 100$
ppb	part per billion
ppb(m/m)	part per billion (molar fraction)
TMB	trimethylbenzene
UBA(A)	Umweltbundesamt GmbH
u_i	uncertainty estimated by the participant for the "i" concentration
u_{lab}	estimated uncertainty for the average value of the 5 measurements of the cylinder
U_{lab}	expanded uncertainty for the average value of the 5 measurements of the cylinder
u_{ref}	uncertainty of the reference value

U_{ref}	expanded uncertainty of the reference value
VMM	Vlaamse Milieumaatschappij
VOC	volatile organic xompound
123TMB	1,2,3 trimethylbenzene
124TMB	1,2,4 trimethylbenzene
135TMB	1,3,5 trimethylbenzene
13BD	1,3 butadiene
1PNE	1, pentene
σ	standard deviation of the 5 individual measurements of the cylinder

Introduction

This report collects the results of the volatile organic compound (VOC) ozone precursors exercise carried out among the National Reference Laboratories of the AQUILA network. This exercise was performed under the umbrella of the new directive 2008/50/EC[(1)]. In addition, EUROMET 886 intercomparison exercise was running in parallel for the relevant laboratory[(2)].

The exercise consisted of the inter-laboratory evaluation of two, ppb concentration level, cylinders: 1) a synthetic VOC mixture and 2) an ambient air mixture. The preparation, distribution, assessment of concentrations and uncertainty calculation, before and after the circulation of the cylinders was the subject of a contract between the Joint Research Centre and the National Physical Laboratories (UK). Therefore, the reference concentrations and associated uncertainties of the circulating cylinders were those determined by the contractor during the course of the exercise.

The data presented in this report have been evaluated according to the proficiency testing scheme for interlaboratory comparisons of ISO 13528, in terms of z-scores[(3)].

This report addresses general observations on the median performance of the laboratories, identifying, where possible, areas for improvement. Individual laboratories can draw inferences on their own performance from the tables of results.

Experimental protocol

The exercise did not impose any particular technique or methodology for sampling or analysis of the VOC under consideration. Each laboratory was free to use one or more techniques for the analysis of the different compounds. However, a detailed description of the applied methodology was requested, as well as an estimation of their analytical uncertainties. Laboratories were asked to report 5 values for each cylinder from 5 different analyses, performed on different days.

Participating laboratories

18 laboratories from the AQUILA network participated in the intercomparison exercise (see Table 1). The distribution of cylinders lasted from the 9 May to 2 July 2007. Cylinders remained on average for three months in the participating laboratories for analysis. The last cylinder was returned at the end of February 2008.

For various reasons some laboratories did not report any results. This was the case for IDA and NERI. The ISCIII provided only an average value and associated uncertainty for the synthetic mixture, while their results for the ambient air mixture were not reported. The CHMI submitted their final analytical results after the time limit for submission: 30 December 2007.

Table 1.- Laboratories accepted for participation in the VOC AQUILA intercomparison exercise

Acronym	Laboratory	Country	Contact
AEAT	AEA Technology	United Kingdom	Steve Telling Peter Dumitrean
EARS	Environmental Agency of The Republic of Slovenia	Slovenia	Rok Brinc Bizjak Mirko
UBA(A)	Umweltbundesamt GmbH	Austria	Marina Fröhlich Claudia Leeb
AOL-UUW	Amt der oberösterreichischen Landesregierung. Abteilung Umweltschutz / Labor	Austria	Adolf Schinerl
CNR	Institute of Atmospheric Pollution, CNR	Italy	Rosanna Mabilia
ISSeP	Institut Scientifique de Service Public	Belgium	GOHY Marie
EMD	National Reference Laboratory (NRL)/ LCSQA Ecole des Mines de Douai	France	LOCOGE Nadine
IVL	Swedish Environmental Research Institute	Sweden	Annika Potter Eva Brorström-Lundén
NPL	National Physical Laboratory	United Kingdom	Martin Milton Peter Woods Paul Quincey Robin Grenfell
ERLAP	European Reference Laboratory of Air Pollution	European Commission	Richard Connolly Natale Cao Pascual Pérez Ballesta
VMM	Vlaamse Milieumaatschappij	Belgium	Eric Wauters Annelies Rogge
EMPA	Empa – Materials Science & Technology. Air Pollution / Environmental Technology	Switzerland	Stefan Reimann
EPA	Environmental Protection Agency	Ireland	Barbara O'Leary Lin Yau Micheál O'Dwyer
FMI	Finnish Meteorological Institute	Finland	Hannele Hakola Heidi Hellen
ISCIII	Instituto de Salud Carlos III	Spain	Rosalia Fernandez Patier
IDA	Laboratório Referência do Ambiente	Portugal	Joao Antonio Soares Silva Matos Joana Brantes Nuno Oteda
NERI	Danmarks Miljøundersøgelser National Environmental Research Institute	Denmark	Axel Egeløv
CHMI	Czech Hydrometeorological Institute	Czech Republic	Jiri Novak

Instrumentation and material

With the exception of EPA which used a BTEX analyser, most of the laboratories reported the 29 compounds requested in the intercomparison. Some of them used more than one instrument dividing the range of hydrocarbons between C2-C6 and C6-C12. Three laboratories used mass spectrometry for the detection and quantification, in particular, over the range of C6-C12.

From the 16 laboratories that reported results, 9 of them were using NPL cylinders as reference calibration material, 2 were using SIAD, 1 NMi, 1 Spectra gases, 2 PRAXAIR and 1 with their own laboratory primary reference. Table 2 shows the main characteristics of the instrumentation and reference material used by each participating laboratory. The full method description provided by each laboratory is given in Annex II.

Table 2.- Reference material and characteristics of the instrumentation

LABORATORY	**Reference Material** (certification date)	**Instrument**
AEAT	NPL (12/2005)	PE TurboMatrix – with Dean Switch system – FID and nafion
EARS	SIAD (3/2006) * expired	Airmovoc – FID
UBA (A)-1	NPL (6/2007)	Airmovoc C2-C6 – FID
UBA (A)-2	NPL (6/2007)	Airmovoc C6-C12 – FID
AOL-UUW	Spectra gases (2/2007) **dilution from high concentration ~ 1000 ppb	PE TurboMatrix – HP6890 MSD TI
CNR	SIAD (8/2007)	Entech cryo-trapping – FID
CNR-MS	SIAD (8/2007)	Chrompack cryo-trapping C6-C12 MS TI
CNR-MSTTI	SIAD (8/2007)	Chrompack cryo-trapping C6-C12 MS TTI
ISSeP	Nmi (8/2005)	PE TurboMatrix – PE GC-MSd Clarus500 TI
EMD	NPL (9/2006)	Chrompack cryo-trapping CP-9001 – with Dean Switch system– FID and nafion
IVL	NPL (1/2006)	Markes Unity – Air server + Varian GC with Dean Switch system– FID and nafion
NPL	NPL (8/2006)	Varian 3600 cryo trapping short glass beads – FID
ERLAP	NPL (9/2006)	PE TurboMatrix – with Dean Switch system FID and nafion
VMM	PRAXAIR (3/2000) *expiried and controlled by primary standard (n.p.) **dilution from high concentration ~ 1000 ppb	PE TurboMatrix and GC (Autosystem XL)– FID
VMM-S1	PRAXAIR (12/2006) **dilution from high concentration ~ 200 ppb	Syntech C6-C12 PID and nafion
VMM-S2	PRAXAIR (12/2006) **dilution from high concentration ~ 200 ppb	Syntech C2-C6 PID+FID and nafion
EMPA	NPL (4/2006)	PE TurboMatrix + HP6890 GC – FID and nafion
EPA	static injection	Syntech C6-C12 PID
FMI	NPL (11/2005)	Canisters to cryo trapping N2 Liquid – Agilent 6890– FID, drier: K2CO3, + NaOH
FMI-MS	NPL (11/2005)	PE TurboMatrix 650 – HP 5972 MSD
ISCIII	PRAXAIR (n.p.) **dilution from high concentration ~ 50 ppb	PE ATD-400 + Finnigan Trace GC ultra – FID
CHMI	NPL (3/2006)	Agilent 6890 – FID with cryotrapping , drier:Silica. Dean Switch system.

(n.p. information not provided).

Circulating cylinders and reference value

The full exercise considered two kinds of mixtures: a synthetic VOC mixture with individual concentrations ranging approximately from 3 to 8 ppb (m/m) and an ambient air mixture with lower concentrations ranging approximately from 0.3 to 4 ppb (m/m).

The components present in the synthetic mixtures and those requested to analyse in the ambient air mixture are given in Table 3. These compounds correspond to hydrocarbons listed in annex VI of the Directive 2002/3/EC relating to the measurement of ozone precursor substances.

Table 3.- List of hydrocarbons considered in the intercomparison exercise

ethane	i-hexane (2-methylpentane)
ethylene (ethene)	hexane
propane	isoprene (2-methyl-1,3-butadiene)
propene	heptane
i-butane (2-methylpropane)	benzene
butane	i-octane (2,2,4-trimethylpentane)
acetylene (ethyne)	octane
trans-2-butene	toluene
1-butene	ethylbenzene
cis-2-butene	m+p-xylene
i-pentane (2-methylbutane)	o-xylene
pentane	1,3,5-trimethylbenzene
1,3-butadiene	1,2,4-trimethylbenzene
trans-2-pentene	1,2,3-trimethylbenzene
1-pentene	

The synthetic gas mixtures were gravimetrically prepared from two distinct "mother" mixtures, named X1 and X2. Mother mixture concentrations ranged from 180 to 380 nmol/mol. Two distinct batches of synthetic mixture cylinders were consequently produced and different reference concentrations attributed to these batches. The cylinders generated by the respective mother mixtures were randomly distributed between laboratories. Table 4 shows the origin of the cylinders received by each laboratory.

Table 4.- Mother mixture used in the manufacture of the cylinder sent to the indicated laboratory

Synthetic mixture X1	Synthetic mixture X2
EARS, UBA (A), AOL-UUW, CNR, ISSeP, EMD, IVL, NPL,ISCIII	AEAT, ERLAP, VMM, EMPA, EPA, FMI, CHMI

The reference concentration for the synthetic mixture was gravimetrically determined and the associated uncertainty was that reported by NPL in their assessment of cylinder stability (see Annex IV)

Table 5 .- Reference concentrations and uncertainties of the circulating cylinders

Compound	Synthetic mixture			Ambient Air Mixture	
	Batch X1, C_{ref} *ppb (m/m)*	*Batch X2,* C_{ref} *ppb (m/m)*	u_{ref}, %	C_{ref} *ppb (m/m)*	u_{ref}, %
ethane	6.74	5.92	0.70	4.09	1.05
ethene	6.69	5.88	0.53	1.99	2.18
propane	6.67	5.86	0.67	2.19	1.66
propene	6.60	5.79	1.03	1.28	2.56
iso-butane	7.10	7.97	1.11	2.00	3.05
n-butane	6.9	7.74	0.78	3.86	1.22
acetylene	6.68	5.86	0.88	2.89	2.54
trans-2-butene	6.89	7.74	0.51	0.70	2.43
1-butene	6.79	7.61	0.68	1.03	2.08
cis-2-butene	6.8	7.63	0.84	0.86	2.27
2-methyl butane	5.12	5.29	0.76	2.51	1.27
n-pentane	5.20	5.37	0.77	1.05	2.57
1,3-butadiene	6.59	5.79	0.63	0.98	2.26
trans-2-pentene	4.95	5.11	0.66	1.30	1.35
1-pentene	5.04	5.21	0.71	0.38	3.41
2-methyl pentane	5.13	5.3	0.78	0.96	3.01
n-hexane	5.14	5.3	0.59	1.04	1.69
isoprene	5.14	5.31	0.60	0.48	2.96
n-heptane	5.07	5.24	0.65	0.83	2.02
benzene	4.18	3.78	0.58	1.66	2.45
2,2,4-trimethyl pentane	5.17	5.34	0.75	0.51	3.17
n-octane	5.12	5.29	0.65	0.35	4.37
toluene	3.59	3.25	0.86	2.20	1.62
ethyl-benzene	3.84	4.22	0.76	0.84	3.06
m+p-xylene	7.59	8.34	0.87	1.86	2.67
o-xylene	3.77	4.14	0.84	0.88	2.62
1,3,5-trimethyl benzene	3.68	4.04	1.08	0.60	4.14
1,2,4-trimethyl benzene	3.86	4.24	1.05	0.79	5.06
1,2,3-trimethyl benzene	3.52	3.86	1.31	0.30	5.30

For the ambient air mixture, the mother stock was made from approximately 1% high concentration, gravimetrically prepared VOC standard and 99% sampled air from Bushy Park, Teddington. The reference concentrations for the ambient air mixture and their corresponding uncertainties were calculated by NPL after analysis of the cylinders before and after circulation, for more details see Annex IV.

Table 5 shows the corresponding reference concentration, C_{ref}, for the synthetic and ambient air mixtures cylinders with their corresponding uncertainties, u_{ref}. The corresponding expanded uncertainty for the reference value U_{ref} was considered as the

reported uncertainty multiplied by a factor of 2. An example of a chromatographic separation for the synthetic and ambient air mixture is given in Annex I.

Evaluation of the laboratory results

Laboratories provided five individual values, C_i, with their corresponding associated uncertainties, u_i, for each compound and cylinder. These data were taken as raw data for the evaluation of the proficiency of the laboratory.

With the exception of those laboratories, which provided average values for the analysis and their corresponding uncertainties (NPL and Carlos III), the five individual results were averaged, $\overline{C_{lab}}$, and the corresponding uncertainty, u_{lab} , calculated according to the following equations:

$$\overline{C_{lab}} = \frac{\sum_{i=1}^{n} C_i}{n} \qquad (1)$$

$$u_{lab} = \sqrt{\frac{\sigma^2 + \sum_{i=1}^{n} u_i^2}{n}} \qquad (2)$$

where n is the number of reported individual analyses, i.e. 5, and σ is the standard deviation of the 5 individual analyses. The 95 % interval of confidence for the expanded uncertainty, U_{lab}, was calculated by multiplying the value u_{lab} from equation (2) by a factor of 2.

In order to evaluate the average results reported by the different laboratories the *En* number as recommended by ISO/EC Guide 43-1:1997, A.2.1.4 item E., was calculated[4]:

$$E_n = \frac{C_{lab} - C_{ref}}{\sqrt{U_{lab}^2 + U_{ref}^2}} \qquad (3)$$

where U_{lab} and U_{ref} are the expanded uncertainties for the reported and reference value, respectively.

E_n number expresses the validity of the expanded uncertainty estimate associated with each result. The critical value for E_n number is 1. E_n numbers higher than 1 identify results that are incompatible with the reference value after allowing for the stated uncertainties. The overall evaluation of the laboratory results should consider both bias and E_n value, because a low *En* value could be due to a large stated uncertainty. Therefore, to indicate performance an overall expanded uncertainty (OEU), representing the sum of the expanded uncertainty of the reported result, U_{lab}, and the absolute value of its bias with respect to the reference value, is used; the relative OEU % being calculated according to the following expression:

$$\left(U_{lab} + \left|\, \overline{C_{lab}} - C_{ref} \,\right|\right) / \overline{C_{lab}} \cdot 100 \qquad (4)$$

Results and discussion

The information collected from each laboratory regarding uncertainty calculation is given in Annex III. Tables 6 and 7 provide the average value and associated uncertainty for the synthetic and ambient air mixture, respectively. With the exception of Carlos III and NPL, who provided average concentration and associated uncertainty, the U_{lab} values were calculated according to equations 1 and 2 from the reported information.

Table 8 and 9 shows the corresponding E_n values and biases with respect to the reference value assigned to the synthetic and ambient air mixture.

Generally, as shown in Figure 1, there is a lower relative uncertainty estimated for the synthetic mixture in comparison with the ambient air mixture for most of the compounds. This is due to the lower concentration level of the ambient air mixture with respect to the synthetic one. A trend of increasing the associated analytical uncertainty is observed with the increase of carbon number. The higher reproducibility uncertainty of the heaviest compounds can be due to several factors: longer times of elution, lower volatilities, memory effect from the adsorbent or due to absorption in the pipe and in the pressure reducer, high blank from the cold trap.

Figure 2 represents the median value for the biases of all participants with respect to the reference value. The trend in the bias from negative to positive with the increase of the carbon number could be due to the lower trapping efficiencies of the lighter compounds. The higher blanks in the system and memory effect observed for the heavier compounds may be the reason for their positive biases.

The analytical difficulties associated with particular compounds can be seen in Figure 3. This represents the percentage of reported data and those under certain thresholds of uncertainty (i.e. relative overall expanded uncertainty, OEU, lower than 5, 10 and 20 %) for the synthetic and ambient air mixture with respect to the total number of participants (in terms of instruments).

Table 6.- Synthetic mixture. Reported average concentration and associated uncertainties (continue)

COMPOUND	AEAT		EARS		UBA (A)-1		UBA (A)-2		AOL-UUW		CNR		CNR-MS		CNR-MSTTI		ISSeP		EMD		IVL	
	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %
ethane	6.05	3.2			5.40	4.4					5.13	4.8							6.84	6.7	5.82	10.0
ethene	5.95	3.1			7.00	20.5					5.22	5.1							6.72	5.7	5.56	7.5
propane	5.95	2.6			6.70	6.1			3.49	20.9	5.56	1.9							6.67	5.5	6.78	5.1
propene	5.87	2.8			6.58	11.8			4.32	11.6	5.71	1.5							6.64	6.0	6.71	5.2
iso-butane	8.01	1.8			7.22	3.2			4.05	21.7	6.14	2.5							7.14	3.2	7.18	6.1
n-butane	7.78	1.9			6.94	3.0			3.89	27.7	6.02	2.1					6.97	31.7	6.86	4.9	6.95	5.0
acetylene	5.89	4.0			6.60	6.0													6.45	9.3	5.03	5.3
trans-2-butene	8.03	7.5			6.90	6.1			5.74	21.7	6.19	2.1					7.26	30.5	6.89	3.1	6.92	7.0
1-butene	7.74	2.7			6.83	4.1			4.05	10.6	5.94	2.3							6.90	3.8	6.63	8.0
cis-2-butene	7.77	2.8			6.86	26.9			3.90	26.7	5.98	1.8					6.73	31.0	6.90	3.7	6.79	6.0
2-methyl butane	5.33	2.1			5.20	16.3			2.88	25.5	4.50	6.1					5.61	15.1	5.15	3.0	5.18	5.0
n-pentane	5.45	34.6			5.26	2.7			2.97	24.3	4.71	15.9					5.64	10.3	5.22	2.9	5.26	5.0
1,3-butadiene	5.99	5.6			7.08	7.5					5.89	2.0					6.84	30.3	6.94	9.1	6.71	32.0
trans-2pentene	5.14	2.0			5.16	8.3			2.68	27.1	5.24	2.9					5.13	15.2	4.98	4.7	4.99	13.0
1-pentene	5.22	2.0			5.18	5.6			2.79	24.9	4.52	11.6							5.08	5.9	5.06	14.0
2-methyl pentane	5.34	2.6			5.10	2.6			3.03	30.3	4.90	20.6					5.32	10.4	5.19	4.9	5.19	5.0
n-hexane	5.32	1.9	23.90	12.1	4.98	8.3			2.94	34.3	4.24	23.7					5.32	15.4	5.20	4.8	5.15	8.0
isoprene	5.50	3.1							2.80	23.1	4.46	13.6					5.05	15.3	5.18	7.0	5.18	13.0
n-heptane	5.29	2.1	28.96	12.0			5.08	4.2	2.57	28.0	4.88	5.7	5.67	25.2	5.50	11.8	5.62	11.2	5.18	4.6	5.10	8.0
benzene			18.32	12.0			4.17	3.4	4.21	12.6	4.15	10.1	4.47	29.3	4.42	33.6	4.79	11.5	4.22	6.7	4.21	9.0
2,2,4-trimethyl pentane	5.37	1.8	33.42	12.0			5.18	4.3	2.87	26.6	5.80	23.3	5.80	23.3	5.81	30.8			5.25	3.3	5.20	5.0
n-octane	5.34	2.1	38.64	12.0			5.12	3.9	2.49	31.2	5.54	14.5	5.54	14.5	4.97	11.0	6.04	13.0	5.32	5.8	5.14	28.0
toluene	3.34	5.0	19.70	12.0			3.57	8.0	1.67	27.2	3.91	8.0	3.73	14.6	3.75	13.4	4.11	13.4	3.62	8.9	3.62	6.0
ethyl-benzene	4.28	3.0	25.96	12.0			3.85	4.2	1.72	28.5	3.84	21.9	3.84	21.9	3.77	23.2	4.44	19.0	4.02	7.5	3.93	6.0
m+p-xylene	8.54	2.8	56.10	12.0			7.60	2.2	3.43	32.9	7.64	21.0	7.64	21.0	7.66	19.1	9.13	20.0	7.87	9.1	7.71	10.0
o-xylene	4.20	3.0	28.19	12.0			3.76	5.5	1.79	31.2	3.80	24.9	3.80	24.9	3.97	32.6	4.67	22.2	3.96	8.9	3.80	9.0
1,3,5-trimethyl benzene	4.12	3.6	39.73	12.0			3.51	4.1	1.90	32.4	3.91	13.4	3.91	13.4	3.84	19.3	4.94	33.3	3.91	9.2	3.83	8.1
1,2,4-trimethyl benzene	4.42	4.7	49.90	12.0			3.61	6.2	2.05	32.8	4.10	19.8	4.10	19.8	4.08	26.3	5.68	35.4	4.11	10.1	4.00	11.1
1,2,3-trimethyl benzene	3.95	3.5	45.84	12.0			3.30	4.6	2.02	13.8	3.96	25.7	3.96	25.7	3.84	18.4			3.76	11.0	3.65	28.1

Table 6.- Synthetic mixture. Reported average concentration and associated uncertainties

COMPOUND	NPL		ERLAP		VMM		VMM-S1		VMM-S2		EMPA		EPA		FMI		FMI-MS		ISCIII		CHMI	
	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %
ethane	6.72	1.2	5.95	3.2					4.98	13.3	6.05	1.4			5.66	4.4			2.42	7.4	5.92	4.9
ethene	6.67	1.1	6.06	4.1					5.25	6.3	5.97	1.0			5.73	13.2			2.80	7.1	5.88	10.0
propane	6.66	1.2	5.86	2.2					6.17	7.3	5.99	1.4			5.61	5.4			2.41	6.6	5.87	5.6
propene	6.54	1.2	5.11	2.1					6.04	5.4	5.92	1.3			5.60	18.2			2.53	7.1	5.81	6.1
iso-butane	7.07	3.1	7.97	3.1	4.86	26.3			8.56	4.1	8.20	1.4			7.53	12.2			2.79	7.2	7.91	7.5
n-butane	6.89	1.1	7.74	3.1	6.77	15.9			6.13	6.1	7.95	1.4			6.65	14.1			2.70	7.0	7.70	6.6
acetylene	6.80	1.7	6.39	4.5					1.34	12.9	6.12	1.6			6.54	18.1			6.02	13.6	5.81	6.9
trans-2-butene	6.88	1.1	7.74	3.2	6.07	13.3			9.54	6.4	7.88	1.3			7.27	19.1			2.69	6.3	7.71	6.6
1-butene	6.79	1.5	7.63	3.5	10.03	26.7			7.29	6.7	7.62	1.4			7.72	28.1			2.69	6.7	7.61	6.5
cis-2-butene	6.78	1.5	7.62	2.8	5.75	13.1			8.70	6.1	7.56	1.5			7.29	19.1			1.70	11.8	7.61	6.6
2-methyl butane	5.13	1.5	5.31	2.7	5.27	7.9			5.77	4.3	5.41	1.5			5.21	15.1			2.56	7.0	5.29	6.2
n-pentane	5.21	1.5	5.38	2.8	5.46	8.2			5.51	5.0	5.49	1.5			5.25	12.2			1.86	7.0	5.39	6.0
1,3-butadiene	6.64	1.6	5.81	2.9					7.21	8.0	5.87	1.6			5.88	19.1			7.04	7.1	5.80	6.6
trans-2pentene	4.93	1.5	5.15	2.5	4.90	7.7			5.96	11.6	5.23	1.4			4.89	19.1			2.08	7.7	5.10	6.4
1-pentene	5.03	1.3	5.23	2.8	5.24	9.7			5.58	10.8	5.30	1.7							2.08	6.3	5.16	6.5
2-methyl pentane	5.13	1.3	5.34	2.5	6.20	26.7			4.49	12.5	5.69	2.7			4.45	26.0					5.31	5.9
n-hexane	5.16	1.3	5.31	1.9	5.97	22.7			4.51	10.7	5.44	1.9			4.90	23.0			1.75	11.4	5.32	8.1
isoprene	5.19	1.6	5.35	3.4	5.42	7.4			6.42	11.0	5.39	1.6			5.46	32.0			4.19	8.6	5.30	6.3
n-heptane	5.06	1.5	5.23	2.0	5.10	10.2	5.21	17.5			5.37	2.0			3.64	33.0					5.28	5.5
benzene	4.18	1.3	3.75	2.3	3.79	9.5	3.50	20.7			3.70	2.5	4.30	22.0			5.05	20.8			3.81	5.4
2,2,4-trimethyl pentane	5.19	1.0	5.34	1.9	5.84	9.1	4.94	20.3			5.82	4.8									5.38	5.6
n-octane	5.15	1.5	5.26	1.8	5.42	9.0	5.08	20.5			5.42	2.2									5.35	5.8
toluene	3.61	2.2	3.28	2.9	3.24	10.5	3.05	20.6			3.24	1.2	2.60	11.5			3.76	20.7			3.32	5.4
ethyl-benzene	3.87	2.4	4.23	2.5	3.99	10.7	4.35	15.3			4.32	3.7	2.62	14.5			4.17	14.2			4.26	5.8
m+p-xylene	7.62	2.2	8.49	3.4	8.36	8.0	8.77	14.8			8.40	3.3	5.10	17.3			8.38	26.5			8.43	5.6
o-xylene	3.77	2.0	4.13	8.8	4.21	7.5	4.58	15.2			4.17	3.9	2.40	19.6			4.29	26.2			4.20	6.1
1,3,5-trimethyl benzene	3.69	2.4	4.18	3.0	4.52	8.2	3.82	18.1			4.15	6.2	2.04	26.9			4.17	20.3			4.08	9.9
1,2,4-trimethyl benzene	3.90	3.3	4.51	9.6	4.86	8.0	4.61	18.5			4.28	7.9					4.37	18.4			4.25	11.3
1,2,3-trimethyl benzene	3.53	2.1	4.07	5.9	4.45	8.1	3.36	20.6			3.89	7.1	2.08	20.8			4.19	18.3			3.87	12.3

Table 7.- Ambient air mixture. Reported average concentration and associated uncertainties (continue)

COMPOUND	AEAT		EARS		UBA (A)-1		UBA (A)-2		AOL-UUW		CNR		CNR-MS		CNR-MSTTI		ISSeP		EMD		IVL	
	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %
ethane	4.10	4.6			4.17	15.5					1.87	7.9							4.00	8.8	4.35	10.0
ethene	1.94	8.4			2.63	22.9					0.54	24.2							1.88	8.2	2.69	9.3
propane	2.21	6.2			2.24	6.3			2.21	7.7	1.54	2.1							2.17	7.4	2.21	5.0
propene	1.33	11.8			1.28	12.4			2.10	33.9	0.91	1.4							1.24	7.7	1.31	6.3
iso-butane	2.02	5.5			1.98	3.1			2.21	6.9	1.58	2.7							2.00	6.1	2.02	6.1
n-butane	3.81	3.5			3.77	2.9			4.01	7.5	3.11	2.4					3.66	34.4	3.53	8.0	3.85	5.0
acetylene	2.67	9.4			3.32	6.4													3.25	10.0	2.71	6.1
trans-2-butene	0.96	62.5			0.67	7.6			1.24	19.2	0.43	3.2					0.80	32.1	0.69	6.1	0.74	7.1
1-butene	1.10	17.9			1.02	4.4			2.24	10.9	0.73	2.0							1.00	5.0	1.04	8.0
cis-2-butene	0.92	22.2			0.50	16.0			1.18	13.8	0.56	2.0					0.92	32.1	0.80	5.4	0.86	6.0
2-methyl butane	2.47	3.9			2.56	15.3			2.65	6.7	1.94	2.6					2.94	16.3	2.43	5.8	2.51	5.0
n-pentane	1.26	139.3			1.05	2.9			1.24	4.2	0.65	2.4					1.24	11.2	1.06	5.8	1.05	5.1
1,3-butadiene	1.08	33.4			0.75	8.0					0.68	3.7					1.00	34.8	0.79	10.3	0.98	32.0
trans-2pentene	1.30	7.4			1.04	8.7			1.35	8.1	0.93	1.4					1.43	15.5	1.30	4.8	1.34	13.0
1-pentene	0.38	25.2			0.25	8.4			0.45	10.3	0.10	5.6							0.35	9.2	0.38	14.2
2-methyl pentane	0.96	14.0			1.16	3.6			1.14	6.8	0.38	11.2					1.13	15.6	1.06	6.9	1.00	5.0
n-hexane	1.04	9.3	4.99	12.0	1.01	14.0			1.14	8.5	0.53	6.4					1.24	18.1	1.07	5.6	1.03	8.5
isoprene	0.46	35.6							0.55	16.0	0.27	7.3					0.59	19.1	0.46	11.0	0.48	13.0
n-heptane	0.91	13.7	4.87	12.1			0.80	11.2	0.90	9.0	0.61	6.5	0.92	23.6	0.92	21.4	0.99	11.0	0.85	7.1	0.83	8.4
benzene			6.20	12.0			1.49	6.6	2.23	14.8	1.16	4.1	1.68	24.6	1.69	28.5	1.99	13.8	1.58	8.9	1.59	9.0
2,2,4-trimethyl pentane	0.58	16.4	3.30	12.0			0.44	4.9	0.62	16.0	0.51	17.4	0.51	17.4	0.53	10.7			0.54	5.7	0.51	5.2
n-octane	0.37	29.8	2.61	12.4			0.35	13.2	0.48	3.9	0.34	31.3	0.34	31.3	0.31	37.7	0.49	16.4	0.35	8.6	0.33	28.0
toluene	2.21	7.3	11.50	12.1			2.09	8.0	2.15	6.8	1.78	7.6	2.30	16.5	2.29	19.2	2.53	13.3	2.14	9.4	2.21	6.0
ethyl-benzene	0.85	15.2	5.59	12.3			0.86	10.7	1.09	6.6	0.86	21.5	0.86	21.5	0.84	22.1	0.99	18.1	0.80	7.6	0.81	6.3
m+p-xylene	1.87	13.0	13.56	12.1			1.89	9.8	2.48	6.1	1.97	23.0	1.97	23.0	2.05	20.4	2.27	18.3	1.73	9.9	1.78	10.7
o-xylene	0.92	13.4	1.86	14.3			0.93	7.4	1.33	5.4	0.92	19.3	0.92	19.3	0.92	27.8	1.11	21.5	0.84	8.5	0.81	9.2
1,3,5-trimethyl benzene	0.59	25.5	6.16	12.2			0.52	10.4	1.34	9.9	0.71	18.9	0.71	18.9	0.63	23.3	0.85	46.3	0.60	10.6	0.61	10.1
1,2,4-trimethyl benzene	0.92	22.8	12.38	12.1			0.77	5.2	1.81	6.1	0.92	30.0	0.92	30.0	0.93	59.1	1.29	43.8	0.77	10.6	0.85	11.3
1,2,3-trimethyl benzene	0.38	36.9	4.90	13.0			0.29	8.6	1.36	13.8	0.42	29.3	0.42	29.3	0.38	17.1			0.29	11.5	0.32	29.9

Table 7.- Ambient air mixture. Reported average concentration and associated uncertainties

COMPOUND	NPL		ERLAP		VMM		VMM-S1		VMM-S2		EMPA		EPA		FMI		FMI-MS		ISCIII		CHMI	
	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %	C_{lab} ppb	U_{lab} %
ethane	4.12	2.6	4.26	3.7					0.63	198.9	4.10	1.4			3.93	4.1					4.13	5.1
ethene	1.98	1.8	1.95	4.3					1.55	25.1	1.90	1.1			1.90	13.0					1.97	19.7
propane	2.19	1.8	2.20	2.1					2.20	6.5	2.14	1.4			2.14	5.1					2.21	6.0
propene	1.30	2.0	1.21	1.5					1.31	14.4	1.20	1.3			1.23	18.0					1.33	7.4
iso-butane	2.06	3.9	1.99	2.3	0.69	52.8			2.20	12.2	1.96	1.5			1.96	12.0					2.02	10.7
n-butane	3.86	2.3	3.81	3.1	2.52	26.5			3.40	10.5	3.77	1.4			3.40	14.1					3.92	6.7
acetylene	2.84	3.6	1.89	6.7					2.20	10.1	2.77	1.6			3.14	18.1					2.90	
trans-2-butene	0.71	1.6	0.70	3.8	0.55	22.6			0.76	12.3	0.69	1.4			0.68	19.0					0.72	8.6
1-butene	1.03	1.5	1.08	3.6	2.00	24.8			1.00	6.0	1.01	1.4			1.06	28.0					1.06	7.5
cis-2-butene	0.86	3.1	0.85	4.1	0.56	27.4			0.92	6.8	0.83	1.6			0.84	19.0					0.88	7.9
2-methyl butane	2.50	1.5	2.47	2.6	2.26	15.7			2.48	10.8	2.46	1.5			2.50	15.2					2.53	6.4
n-pentane	1.07	2.0	1.04	3.6	1.05	15.2			1.04	14.8	1.04	1.6			1.04	12.2					1.09	6.9
1,3-butadiene	0.96	2.4	0.99	4.4					1.14	18.3	0.96	1.8			1.03	19.0					1.01	7.6
trans-2pentene	1.28	2.5	1.30	2.7	1.14	17.1			1.40	13.8	1.28	1.4			1.30	19.0					1.40	7.0
1-pentene	0.39	5.2	0.38	10.7	0.46	31.0			0.53	12.6	0.56	1.8									0.37	13.1
2-methyl pentane	1.00	6.8	1.01	3.0	0.99	15.8			0.94	10.1	0.92	2.4			1.01	26.1					1.00	7.2
n-hexane	1.03	1.6	1.06	2.9	1.01	10.3			1.05	20.9	1.00	1.9			1.00	23.0					1.05	11.1
isoprene	0.49	2.7	0.49	10.0	0.47	21.8			0.53	27.9	0.53	1.8			0.51	32.1					0.50	10.6
n-heptane	0.87	3.3	0.91	4.8	0.81	10.2	0.53	7.5			0.80	3.6			0.73	28.2					0.85	7.4
benzene	1.66	2.8	1.60	3.0	1.49	11.0	1.69	3.7			1.47	2.6	1.22	19.7			2.65	20.9			1.56	5.8
2,2,4-trimethyl pentane	0.51	3.6	0.55	7.3	0.54	9.1	0.77	6.5			0.37	4.8									0.54	9.2
n-octane	0.36	4.8	0.45	8.1	0.35	8.8	0.29	7.2			0.29	2.4									0.36	12.6
toluene	2.19	3.2	2.22	2.7	2.09	12.0	2.51	3.9			2.10	1.3	2.32	33.1			2.52	21.1			2.20	5.5
ethyl-benzene	0.86	3.5	1.01	5.6	0.76	8.8	0.70	6.3			0.79	3.8	0.92	28.2			0.78	14.4			0.81	7.4
m+p-xylene	1.91	3.8	2.21	7.8	1.79	7.4	1.76	7.4			1.79	3.4	1.92	25.2			1.77	26.6			1.81	6.3
o-xylene	0.89	5.1	1.07	10.9	0.85	8.2	0.84	6.1			0.86	4.2	0.96	36.4			0.87	26.3			0.86	7.5
1,3,5-trimethyl benzene	0.64	4.0	0.94	16.0	0.64	10.5	0.55	11.6			0.57	6.9	0.92	42.5			0.54	20.7			0.59	10.1
1,2,4-trimethyl benzene	0.84	4.4	1.27	15.6	0.89	8.8	1.18	10.6			0.88	8.0					0.78	18.5			0.78	9.6
1,2,3-trimethyl benzene	0.33	4.1	0.86	23.2	0.34	8.9	0.22	24.3			0.41	9.8	1.34	38.5			0.31	18.4			0.33	15.2

Table 8.- Synthetic mixture. En number and bias with respect to the reference value (continue)

COMPOUND	AEAT		EARS		UBA (A)-1		UBA (A)-2		AOL-UUW		CNR		CNR-MS		CNR-MSTTI		ISSeP		EMD		IVL	
	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %
ethane	0.6	2.2			-5.3	-19.9					-6.1	-23.8							0.2	1.5	-1.6	-13.7
ethene	0.4	1.2			0.2	4.6					-5.4	-22.0							0.1	0.4	-2.7	-16.9
propane	0.5	1.6			0.1	0.5			-4.3	-47.6	-8.2	-16.7							0.0	0.0	0.3	1.7
propene	0.4	1.4			0.0	-0.3			-4.4	-34.6	-5.5	-13.5							0.1	0.5	0.3	1.7
iso-butane	0.2	0.5			0.4	1.7			-3.4	-43.0	-4.4	-13.5							0.1	0.5	0.2	1.1
n-butane	0.2	0.5			0.2	0.8			-2.8	-43.5	-5.1	-12.6					0.0	1.2	-0.1	-0.4	0.2	0.9
acetylene	0.1	0.5			-0.2	-1.2													-0.4	-3.5	-5.7	-24.7
trans-2-butene	0.5	3.7			0.0	0.2			-0.9	-16.7	-4.7	-10.2					0.2	5.4	0.0	0.0	0.1	0.4
1-butene	0.6	1.8			0.1	0.6			-6.3	-40.4	-5.2	-12.6							0.4	1.6	-0.3	-2.3
cis-2-butene	0.6	1.8			0.0	0.9			-2.8	-42.7	-5.2	-12.1					0.0	-1.0	0.4	1.5	0.0	-0.2
2-methyl butane	0.3	0.7			0.1	1.6			-3.0	-43.7	-2.2	-12.1					0.6	9.6	0.2	0.7	0.2	1.2
n-pentane	0.0	1.6			0.4	1.2			-3.1	-42.8	-0.6	-9.4					0.7	8.5	0.1	0.4	0.2	1.1
1,3-butadiene	0.6	3.5			0.9	7.5					-4.9	-10.7					0.1	3.8	0.5	5.3	0.1	1.8
trans-2pentene	0.2	0.5			0.5	4.3			-3.1	-45.9	1.7	5.9					0.2	3.5	0.1	0.6	0.1	0.8
1-pentene	0.1	0.2			0.5	2.9			-3.2	-44.6	-1.0	-10.2							0.1	0.8	0.0	0.4
2-methyl pentane	0.3	0.8			-0.2	-0.6			-2.3	-40.9	-0.2	-4.4					0.3	3.7	0.2	1.1	0.2	1.1
n-hexane	0.2	0.4	6.5	366.0	-0.4	-2.9			-2.2	-42.8	-0.9	-17.3					0.2	3.7	0.3	1.4	0.0	0.3
isoprene	1.0	3.6							-3.6	-45.4	-1.1	-13.2					-0.1	-1.8	0.1	0.8	0.1	0.7
n-heptane	0.4	1.0	6.9	471.2			0.0	0.2	-3.5	-49.3	-0.7	-3.7	0.4	11.8	0.7	8.5	0.9	10.9	0.4	2.1	0.1	0.6
benzene			6.4	338.3			-0.1	-0.3	0.1	0.8	-0.1	-0.7	0.2	6.9	0.2	5.7	1.1	14.6	0.1	1.0	0.1	0.8
2,2,4-trimethyl pentane	0.3	0.6	7.0	546.4			0.1	0.2	-3.0	-44.5	0.5	12.3	0.5	12.3	0.4	12.5			0.4	1.5	0.1	0.6
n-octane	0.4	1.0	7.2	654.7			0.0	0.0	-3.4	-51.3	0.5	8.2	0.5	8.2	-0.3	-2.9	1.2	17.9	0.6	3.9	0.0	0.5
toluene	0.5	2.9	6.8	448.8			-0.1	-0.6	-4.2	-53.6	1.0	9.0	0.2	3.8	0.3	4.4	0.9	14.4	0.1	0.9	0.1	0.8
ethyl-benzene	0.4	1.4	7.1	576.0			0.0	0.2	-4.3	-55.3	0.0	-0.1	0.0	-0.1	-0.1	-1.9	0.7	15.7	0.6	4.8	0.4	2.2
M+p-xylene	0.7	2.3	7.2	639.2			0.0	0.1	-3.7	-54.8	0.0	0.6	0.0	0.6	0.1	1.0	0.8	20.3	0.4	3.7	0.2	1.6
o-xylene	0.4	1.5	7.2	647.7			0.0	-0.3	-3.5	-52.6	0.0	0.8	0.0	0.8	0.2	5.3	0.9	24.0	0.5	5.0	0.1	0.9
1,3,5-trimethyl benzene	0.5	2.0	7.6	979.8			-1.1	-4.7	-2.9	-48.4	0.4	6.4	0.4	6.4	0.2	4.5	0.8	34.3	0.6	6.2	0.5	4.0
1,2,4-trimethyl benzene	0.8	4.1	7.7	1192.7			-1.1	-6.5	-2.7	-46.9	0.3	6.2	0.3	6.2	0.2	5.7	0.9	47.1	0.6	6.4	0.3	3.6
1,2,3-trimethyl benzene	0.6	2.5	7.7	1202.4			-1.2	-6.1	-5.1	-42.7	0.4	12.4	0.4	12.4	0.4	9.1			0.6	6.8	0.1	3.8

*in red E_n values ≥ 1 and bias $[(C_{lab}-C_{ref})/C_{ref}.100] \geq 10$ %

Table 8.- Synthetic mixture. En number and bias with respect to the reference value

COMPOUND	NPL		ERLAP		VMM		VMM-S1		VMM-S2		EMPA		EPA		FMI		FMI-MS		ISCIII		CHMI	
	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %
ethane	-0.2	-0.3	0.2	0.6					-1.4	-15.8	1.1	2.3			-1.0	-4.5			-21.3	-64.1	0.0	0.1
ethene	-0.2	-0.2	0.7	3.0					-1.9	-10.7	1.0	1.5			-0.2	-2.5			-18.3	-58.1	0.0	0.0
propane	-0.1	-0.2	0.0	0.1					0.7	5.2	1.2	2.3			-0.8	-4.3			-23.2	-63.9	0.0	0.2
propene	-0.4	-0.9	-4.2	-11.8					0.7	4.4	0.9	2.3			-0.2	-3.2			-18.0	-61.7	0.1	0.4
Iso-butane	-0.1	-0.4	0.0	0.0	-2.4	-39.0			1.5	7.4	1.1	2.9			-0.5	-5.5			-16.9	-60.7	-0.1	-0.7
n-butane	0.0	0.1	0.0	0.0	-0.9	-12.5			-4.1	-20.8	1.3	2.8			-1.1	-14.1			-19.2	-60.8	-0.1	-0.5
acetylene	0.8	1.9	1.7	9.1					-22.4	-77.1	1.8	4.4			0.6	11.6			-0.8	-9.9	-0.1	-0.9
trans-2-butene	-0.1	-0.1	0.0	0.0	-2.1	-21.5			2.9	23.3	1.1	1.9			-0.3	-6.0			-22.8	-61.0	-0.1	-0.4
1-butene	0.0	0.0	0.1	0.3	0.9	31.8			-0.6	-4.2	0.1	0.1			0.1	1.4			-20.3	-60.4	0.0	-0.1
cis-2-butene	-0.1	-0.3	-0.1	-0.2	-2.5	-24.6			2.0	14.0	-0.4	-0.9			-0.2	-4.5			-22.1	-75.0	0.0	-0.3
2-methyl butane	0.1	0.3	0.1	0.3	0.0	-0.3			1.8	9.0	1.1	2.3			-0.1	-1.6			-13.1	-50.0	0.0	0.1
n-pentane	0.1	0.2	0.1	0.3	0.2	1.7			0.5	2.6	1.0	2.2			-0.2	-2.2			-21.9	-64.2	0.1	0.3
1,3-butadiene	0.4	0.7	0.1	0.4					2.5	24.5	0.7	1.4			0.1	1.6			0.9	6.8	0.0	0.1
trans-2pentene	-0.2	-0.4	0.3	0.8	-0.5	-4.1			1.2	16.6	1.2	2.3			-0.2	-4.3			-16.6	-58.0	0.0	-0.2
1-pentene	-0.1	-0.2	0.1	0.4	0.1	0.6			0.6	7.2	0.7	1.7							-19.9	-58.7	-0.2	-1.0
2-methyl pentane	0.0	0.1	0.2	0.7	0.5	16.9			-1.4	-15.4	2.3	7.4			-0.7	-16.1					0.0	0.2
n-hexane	0.3	0.6	0.1	0.2	0.5	12.7			-1.6	-14.9	1.2	2.7			-0.4	-7.6			-16.2	-65.9	0.0	0.4
isoprene	0.5	1.0	0.2	0.7	0.3	2.2			1.6	20.9	0.8	1.6			0.1	2.9			-2.6	-18.5	0.0	-0.3
n-heptane	-0.1	-0.2	-0.1	-0.2	-0.3	-2.7	0.0	-0.6			1.0	2.4			-1.3	-30.5					0.1	0.7
benzene	-0.1	-0.1	-0.3	-0.8	0.0	0.3	-0.4	-7.3			-0.7	-2.0	0.5	13.8			1.2	33.5			0.1	0.7
2,2,4-trimethyl pentane	0.2	0.4	0.0	0.0	0.9	9.4	-0.4	-7.5			1.6	9.0									0.1	0.8
n-octane	0.3	0.6	-0.2	-0.5	0.3	2.4	-0.2	-4.0			0.9	2.5									0.2	1.2
toluene	0.2	0.5	0.3	1.0	0.0	-0.4	-0.3	-6.1			-0.1	-0.2	-2.1	-20.0			0.7	15.6			0.4	2.2
ethyl-benzene	0.3	0.8	0.1	0.2	-0.5	-5.5	0.2	3.2			0.6	2.5	-4.2	-37.9			-0.1	-1.1			0.2	1.0
m+p-xylene	0.1	0.4	0.5	1.8	0.0	0.3	0.3	5.2			0.2	0.7	-3.6	-38.8			0.0	0.4			0.2	1.1
o-xylene	0.0	0.0	0.0	-0.2	0.2	1.8	0.6	10.6			0.2	0.7	-3.7	-42.0			0.1	3.7			0.2	1.6
1,3,5-trimethyl benzene	0.1	0.2	0.9	3.4	1.3	11.8	-0.3	-5.4			0.4	2.6	-3.6	-49.5			0.2	3.3			0.1	1.1
1,2,4-trimethyl benzene	0.2	1.0	0.6	6.3	1.5	14.6	0.4	8.7			0.1	0.9					0.2	3.1			0.0	0.4
1,2,3-trimethyl benzene	0.1	0.3	0.8	5.3	1.6	15.4	-0.7	-13.0			0.1	0.7	-4.0	-46.1			0.4	8.6			0.0	0.3

*in red E_n values $\geq$ 1 and bias $[(C_{lab}-C_{ref})/C_{ref}.100] \geq 10$ %

Table 9.- Ambient air mixture. Reported average concentrations and associated uncertainties (continue)

COMPOUND	AEAT		EARS		UBA (A)-1		UBA (A)-2		AOL-UUW		CNR		CNR-MS		CNR-MSTTI		ISSeP		EMD		IVL	
	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %
ethane	0.0	0.1			0.1	1.9					-13.0	-54.3							-0.2	-2.1	0.6	6.2
ethene	-0.3	-2.4			1.0	32.1					-9.3	-73.0							-0.6	-5.6	2.6	35.1
propane	0.1	0.7			0.3	2.1			0.1	0.5	-8.2	-29.8							-0.2	-1.2	0.1	0.6
propene	0.3	3.5			-0.1	-0.7			1.1	63.1	-5.5	-28.9							-0.4	-3.2	0.3	2.3
iso-butane	0.1	0.8			-0.2	-1.1			1.1	10.6	-3.3	-21.1							0.0	-0.1	0.1	1.1
n-butane	-0.3	-1.3			-0.6	-2.4			0.5	3.9	-6.3	-19.5					-0.2	-5.2	-1.1	-8.6	-0.1	-0.3
acetylene	-0.7	-7.5			1.7	14.9													1.0	12.4	-0.8	-6.2
trans-2-butene	0.4	36.7			-0.5	-4.7			2.2	75.6	-7.4	-38.6					0.4	14.0	-0.2	-1.6	0.5	4.3
1-butene	0.4	7.0			-0.2	-1.0			4.9	117.5	-6.7	-29.3							-0.4	-2.5	0.1	0.6
cis-2-butene	0.3	7.5			-4.0	-41.9			1.9	37.4	-7.3	-34.5					0.2	6.8	-1.0	-6.5	0.0	0.1
2-methyl butane	-0.4	-1.9			0.1	1.8			0.7	5.3	-7.1	-23.0					0.9	16.8	-0.5	-3.4	0.0	-0.2
n-pentane	0.1	19.4			-0.1	-0.9			2.4	17.2	-7.3	-38.8					1.3	17.8	0.0	0.1	0.0	-0.3
1,3-butadiene	0.3	9.3			-3.1	-23.7					-6.0	-31.2					0.0	1.2	-2.1	-19.8	0.0	-0.3
trans-2pentene	0.0	-0.1			-2.7	-19.8			0.4	3.7	-9.8	-28.3					0.6	10.3	0.1	0.3	0.2	2.7
1-pentene	-0.1	-2.3			-4.2	-36.1			1.2	16.9	-10.6	-73.8							-0.9	-10.1	-0.1	-1.6
2-methyl pentane	0.0	0.3			2.8	20.6			1.9	19.2	-8.0	-60.0					0.9	18.1	1.1	10.2	0.5	3.8
n-hexane	-0.1	-0.9	6.6	377.3	-0.2	-3.0			1.0	9.5	-10.5	-49.2					0.9	18.7	0.3	2.0	-0.1	-1.1
isoprene	-0.1	-4.7							0.7	14.2	-6.1	-44.0					0.9	20.7	-0.5	-5.6	0.0	-0.3
n-heptane	0.6	9.4	6.8	487.1			-0.4	-4.1	0.8	8.0	-4.1	-26.0	0.4	10.7	0.4	10.8	1.4	19.6	0.3	2.4	0.0	0.1
benzene			6.1	273.5			-1.3	-10.1	1.7	34.5	-5.3	-30.2	0.1	1.4	0.1	2.1	1.2	20.1	-0.5	-4.8	-0.4	-4.4
2,2,4-trimethyl pentane	0.7	13.7	7.0	547.8			-1.9	-14.1	1.1	22.4	0.0	-0.6	0.0	-0.6	0.3	3.4			0.6	5.5	0.0	-0.1
n-octane	0.1	4.5	7.0	645.2			0.0	-0.6	3.5	36.0	-0.1	-2.0	-0.1	-2.0	-0.4	-12.4	1.7	41.0	0.0	0.0	-0.2	-4.5
toluene	0.1	0.7	6.7	422.5			-0.6	-5.1	-0.3	-2.5	-2.7	-18.9	0.3	4.5	0.2	4.1	1.0	14.9	-0.3	-2.5	0.1	0.6
ethyl-benzene	0.0	0.2	6.9	561.7			0.1	1.3	2.8	29.0	0.1	1.7	0.1	1.7	0.0	-0.4	0.8	17.7	-0.6	-5.3	-0.5	-4.2
m+p-xylene	0.0	0.4	7.1	627.0			0.1	1.6	3.4	33.1	0.2	5.8	0.2	5.8	0.4	9.7	0.9	21.5	-0.7	-7.3	-0.4	-4.8
o-xylene	0.3	3.9	3.6	109.7			0.5	4.9	5.2	50.3	0.2	3.8	0.2	3.8	0.2	4.4	0.9	25.2	-0.6	-5.3	-0.8	-8.4
1,3,5-trimethyl benzene	-0.1	-1.8	7.4	917.6			-1.2	-14.0	5.2	122.1	0.7	16.9	0.7	16.9	0.2	4.1	0.6	40.7	0.0	-0.2	0.1	1.3
1,2,4-trimethyl benzene	0.5	15.4	7.7	1457.6			-0.3	-3.4	7.4	127.7	0.4	15.6	0.4	15.6	0.2	16.7	0.9	62.3	-0.2	-2.9	0.4	6.6
1,2,3-trimethyl benzene	0.5	24.5	7.2	1507.4			-0.3	-4.3	5.5	346.6	0.9	37.2	0.9	37.2	1.0	23.0			-0.4	-6.2	0.1	4.8

*in red E_n values ≥ 1 and bias $[(C_{lab}-C_{ref})/C_{ref}.100] \geq 10$ %

Table 9.- Ambient air mixture. Reported average concentrations and associated uncertainties

COMPOUND	NPL		ERLAP		VMM		VMM-S1		VMM-S2		EMPA		EPA		FMI		FMI-MS		ISCIII		CHMI	
	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %	En	Bias %
ethane	0.1	0.3	0.9	4.1					-2.7	-84.5	0.1	0.3			-0.9	-3.8					0.2	1.1
ethene	-0.3	-1.4	-0.4	-2.2					-1.1	-22.0	-1.0	-4.6			-0.3	-4.6					**0.0**	**-0.8**
propane	0.0	-0.2	0.0	0.1					0.0	0.2	-0.8	-2.7			-0.4	-2.3					0.1	0.9
propene	0.0	-0.1	-1.0	-5.6					0.1	2.3	-1.2	-6.5			-0.3	-4.7					0.4	3.8
Iso-butane	0.3	2.4	-0.1	-0.6	-3.4	-65.4			0.7	10.0	-0.3	-1.9			-0.1	-1.8					**0.1**	**0.8**
n-butane	0.0	-0.1	-0.4	-1.5	-2.0	-34.8			-1.3	-12.0	-0.9	-2.5			-1.0	-12.0					0.2	1.4
acetylene	0.0	0.1	-5.1	-34.5					-2.6	-23.9	-0.8	-4.2			0.4	8.6						**0.2**
trans-2-butene	0.1	0.4	-0.2	-1.2	-1.2	-22.5			0.5	7.5	-0.5	-2.5			-0.2	-3.3					0.2	1.8
1-butene	0.1	0.5	0.8	4.6	2.0	94.5			-0.4	-3.0	-0.5	-2.1			0.1	3.0					0.4	3.1
Cis-2-butene	-0.2	-1.3	-0.2	-1.4	-1.9	-34.5			0.9	7.4	-0.8	-4.0			-0.1	-2.8					0.2	2.1
2-methyl butane	-0.1	-0.4	-0.5	-1.8	-0.7	-10.2			-0.1	-1.5	-0.7	-2.0			0.0	-0.7					0.1	0.5
n-pentane	0.2	0.9	-0.3	-1.6	0.0	-0.1			-0.1	-1.2	-0.3	-1.6			-0.1	-1.0					0.3	3.0
1,3-butadiene	-0.2	-1.0	0.0	0.2					0.7	15.7	-0.6	-2.7			0.2	5.0					0.3	2.9
trans-2pentene	-0.2	-0.9	0.1	0.3	-0.8	-12.4			0.5	7.5	-0.5	-1.5			0.0	0.4					0.9	7.5
1-pentene	-0.2	-1.7	-0.1	-1.5	0.5	20.5			2.0	38.1	6.1	44.4									-0.3	-4.1
2-methyl pentane	0.3	2.5	0.7	5.0	0.2	2.6			-0.2	-2.2	-0.6	-3.7			0.2	4.9					0.5	4.4
n-hexane	-0.2	-0.8	0.3	1.6	-0.3	-3.4			0.0	0.5	-1.1	-4.3			-0.2	-4.5					0.0	0.5
isoprene	0.2	1.2	0.1	1.4	-0.1	-2.3			0.3	9.8	1.6	9.9			0.2	5.2					0.2	2.6
n-heptane	0.5	2.8	1.4	9.1	-0.2	-1.9	-5.8	-36.4			-0.7	-3.6			-0.5	-12.6					0.2	1.9
benzene	-0.3	-1.5	-0.6	-3.3	-0.9	-10.0	0.3	2.0			-2.1	-11.5	-1.7	-26.5			1.8	59.3			-0.8	-5.7
2,2,4-trimethyl pentane	0.1	0.4	0.8	7.6	0.5	5.9	4.3	50.5			-3.7	-26.6									0.6	6.8
n-octane	0.2	2.3	2.1	28.8	0.1	1.4	-1.6	-16.6			-1.9	-17.0									0.3	4.2
toluene	-0.2	-0.7	0.3	1.1	-0.4	-4.8	2.5	13.9			-1.3	-4.4	0.2	5.5			0.6	14.3			0.0	0.1
ethyl-benzene	0.0	-0.3	2.1	19.3	-1.0	-9.6	-2.2	-17.7			-1.0	-6.9	0.3	8.9			-0.5	-7.2			-0.4	-4.0
m+p-xylene	0.1	0.6	1.8	18.6	-0.5	-4.2	-0.7	-5.8			-0.6	-3.9	0.1	2.9			-0.2	-5.3			-0.4	-2.9
o-xylene	0.0	0.2	1.4	20.4	-0.4	-3.6	-0.6	-4.8			-0.4	-2.9	0.2	8.5			-0.1	-2.1			-0.3	-2.3
1,3,5-trimethyl benzene	0.5	4.7	2.1	56.1	0.4	5.0	-0.6	-8.4			-0.5	-5.0	0.8	52.1			-0.5	-10.0			-0.2	-2.4
1,2,4-trimethyl benzene	0.3	3.8	2.2	59.4	0.8	11.9	2.6	48.1			0.8	10.2					-0.1	-1.7			-0.1	-2.0
1,2,3-trimethyl benzene	0.5	6.3	2.7	182.1	0.7	10.4	-1.3	-27.0			2.0	33.8	2.0	339.3			0.1	1.3			0.5	9.7

*in red E_n values $\geq$ 1 and bias $[(C_{lab}-C_{ref})/C_{ref}.100] \geq 10$ %

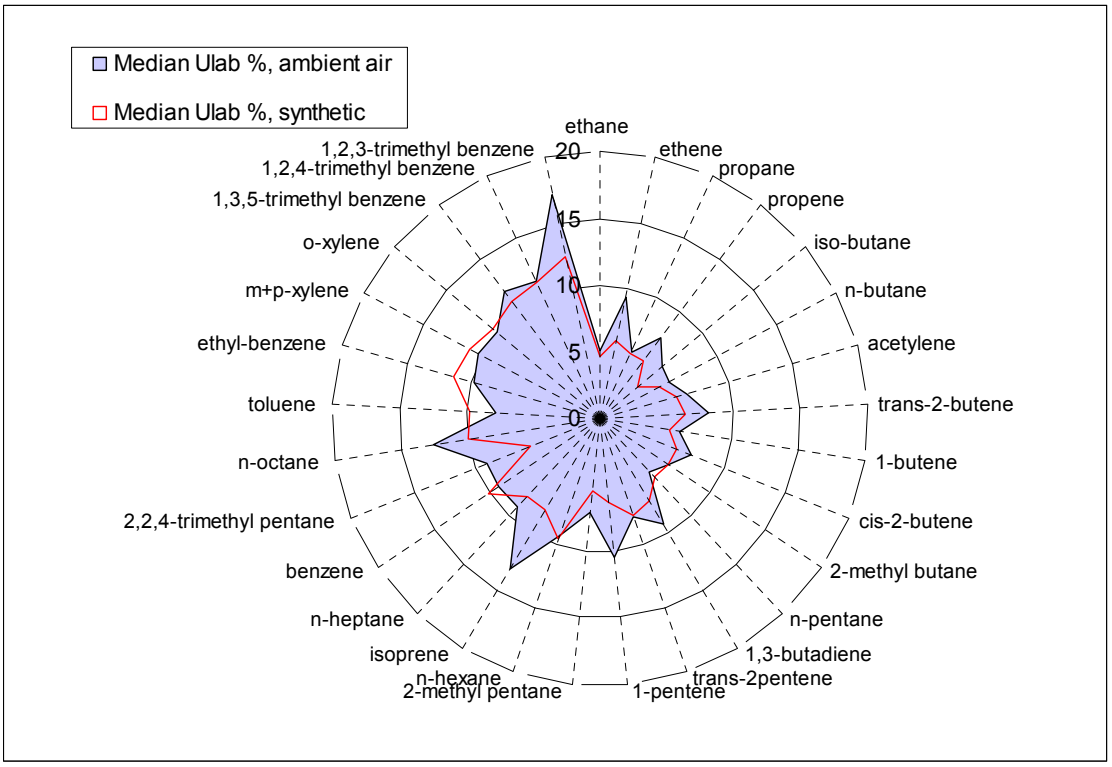


Figure 1.- Median values for the associated relative expanded uncertainties of the reported concentrations of the synthetic and ambient air mixture

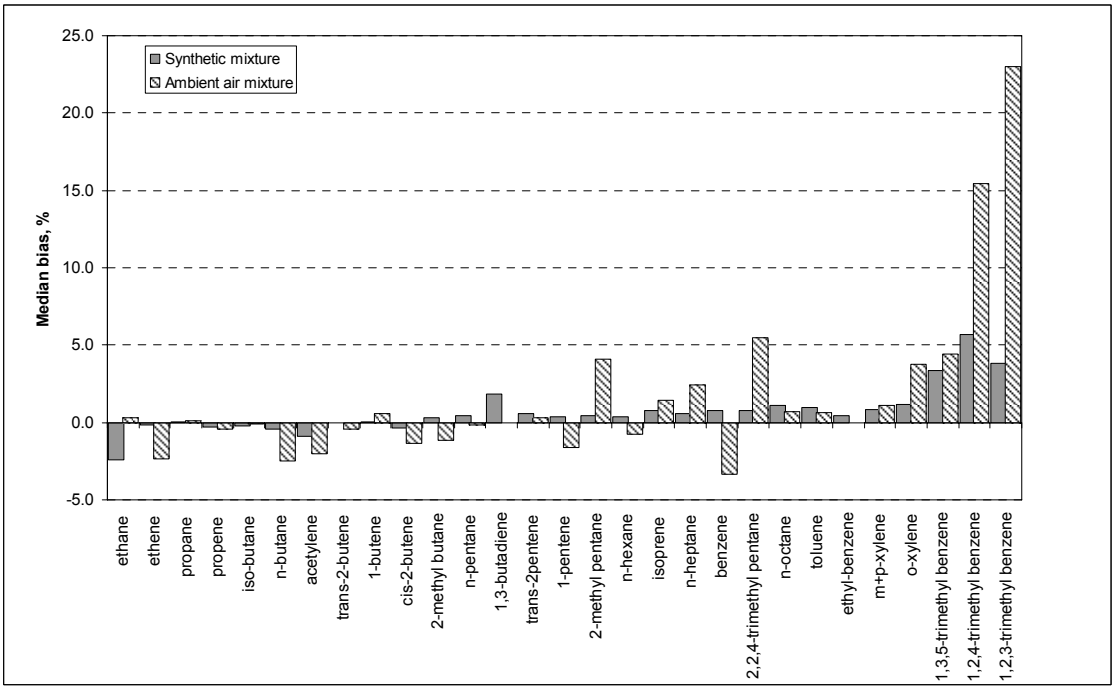


Figure 2.- Median bias with respect to the reference value

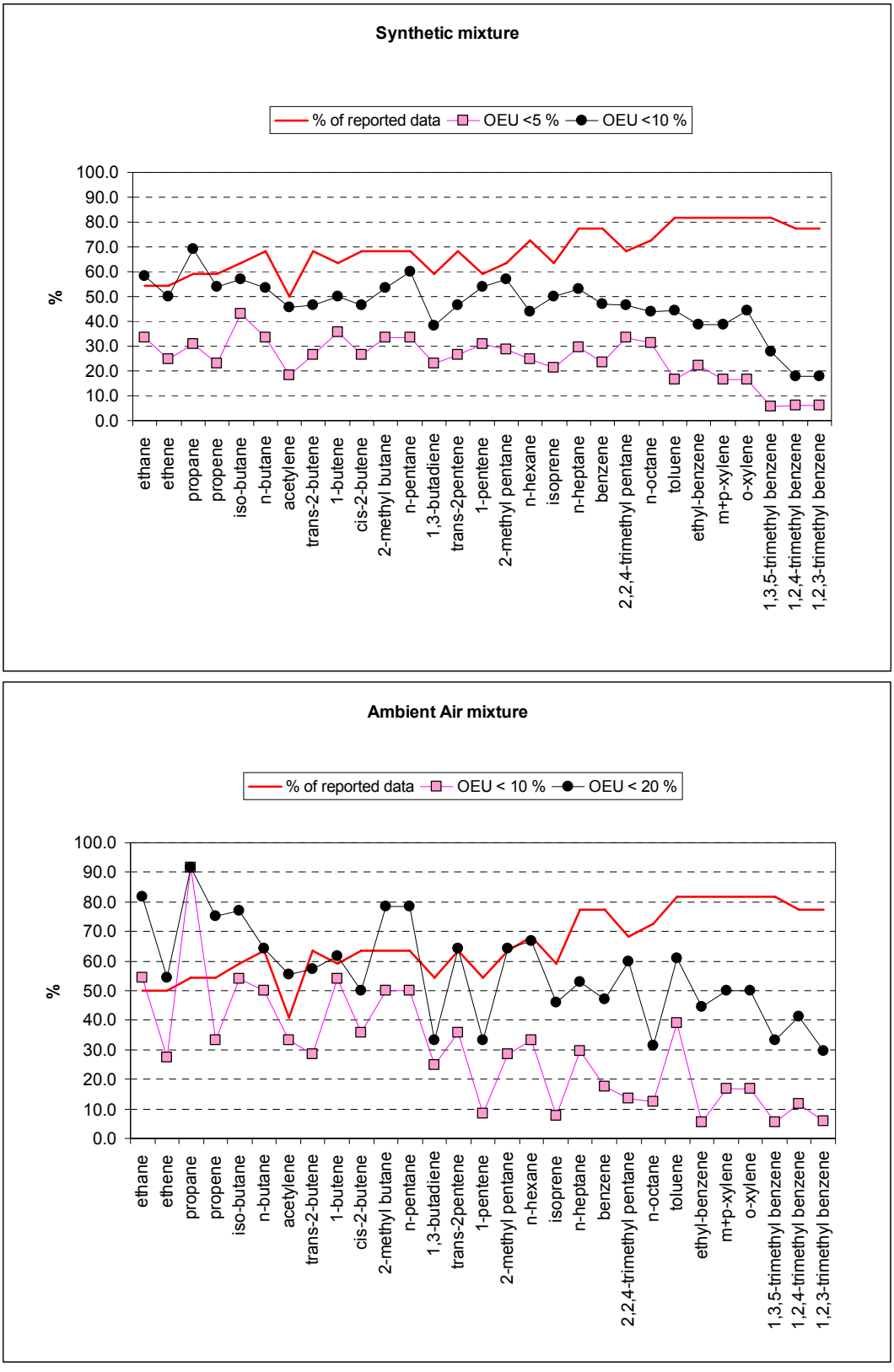


Figure 3.- General performance of laboratory as a function of the compound for the synthetic and ambient air mixture

Figure 3 shows that those compounds with the lower percentage of data reporting correspond to the lighter hydrocarbons. In particular, ethane, ethane, propane, propene, 1,3 butadiene and 1 pentene (with percentages under 60 %) for the synthetic mixture and ethane, ethene and acetylene (with percentages under 50 %) for the ambient air mixture. This is indicative of the higher technical difficulties linked to the analysis of the lighter hydrocarbons in comparison to the heavier ones. In terms of uncertainty the situation is the opposite: the heavier hydrocarbons seem to be analysed with a higher uncertainty than the lighter hydrocarbons. Nevertheless, there is a correlation between relative OEU and concentration level, which is reflected in the graph from Figure 4 for both synthetic and ambient air mixtures.

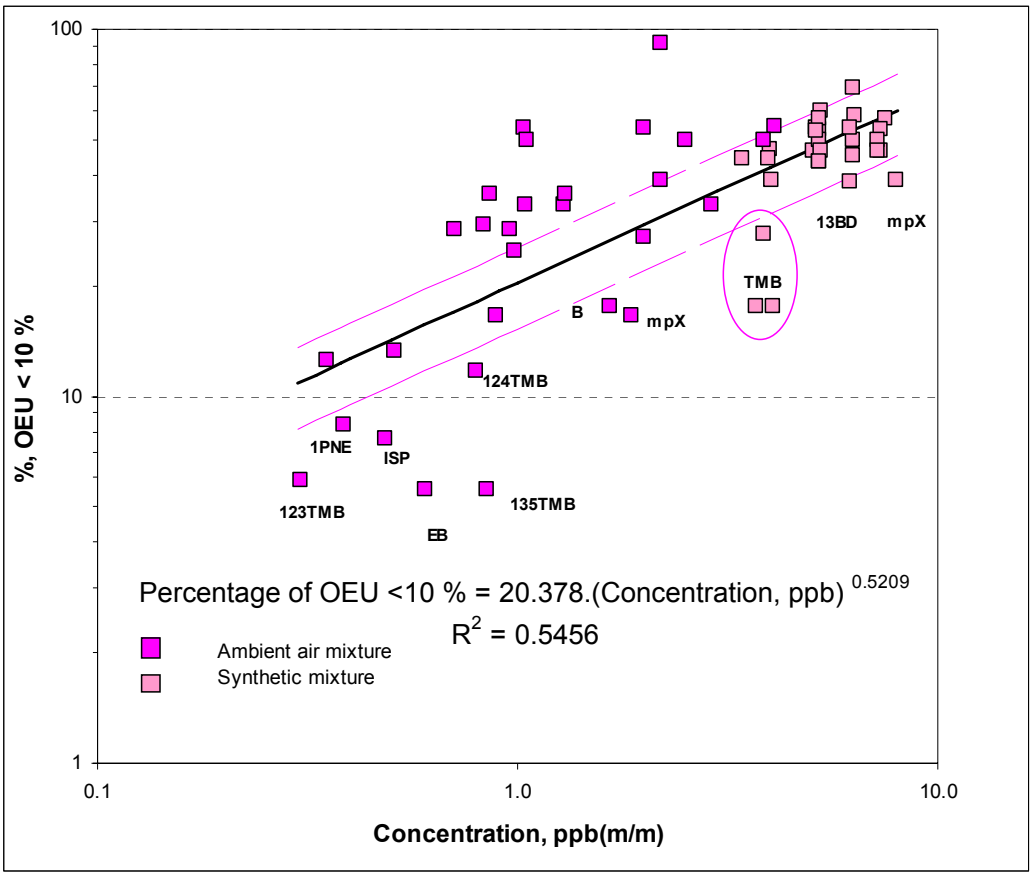


Figure 4 .- Percentage of data with a relative overall expanded uncertainty lower than 10 % as a function of the concentration level

The percentage of reported data with a relative OEU lower than 10 % and concentration is best correlated through a power equation in Figure 4, where those compounds that differ more than 25 % from the correlation trend are also visible. These compounds can considered as difficult to analyse in comparison to the other analytes of the mixture independently of the concentration level effect. This was the case for the trimethyl benzene, mp-xylene and 1,3 butadiene in the synthetic mixture and the trimethyl benzene, m,p-xylene, ethyl benzene, benzene, 1-pentene and isoprene in the ambient air mixture.

Conclusions

Among the 38 reference laboratories and research institutes from the 29 different countries (members of the AQUILA network), only 18 laboratories from 15 countries participated in the current exercise. Two of the participating laboratories did not report any result at the end of the exercise.

Regarding the instrumentation used by the participants, approximately half of the laboratories were using a drier, the most common cooling system was based on Peltier effect as opposed to the cryofocusing technique, broadly used in previous exercises. Dual column systems with double detectors were also used by several participants. Flame ionization detector was the most common detector used, whilst mass spectrometry was used by only a few laboratories.

Most of the participating laboratories used certified reference materials, i.e. cylinders, provided by NPL. This may have an effect on the improvement of the average performance of the laboratories, which may not represent the current situation of reproducibility of the reference material and cylinder stability in the market.

In general, there is a trend of increasing uncertainties for the measurements of compounds with a higher number of carbons, i.e. the heavier hydrocarbons were reported with higher uncertainties than the lighter compounds. This was observed for both synthetic and ambient air mixtures. Furthermore, the concentrations given by the participants for the ambient air mixture were commonly characterised by higher uncertainties in comparison to the data reported for the synthetic mixture.

For both synthetic and ambient air mixtures, the median value of the biases with respect to the reference value determined by the cylinder producer tended to move from negative to positive with an increase in the carbon number of the hydrocarbon.

Although the number of reporting data by the participating laboratories increases with the carbon number of the compound, the quality of the results decreases. The overall uncertainty associated with the heaviest compounds is higher than that calculated for the lighter hydrocarbons.

The concentration level is clearly affecting the overall expanded uncertainty of the analytical results. For the synthetic mixture with an average concentration level of circa 5 ppb, half of the laboratories were reporting OEU better than 10 %. Whilst, for the ambient air mixture with an average concentration of circa 1 ppb, the same percentage of laboratory showed only relative OEU better than 20 %.

Independent of the concentration level some compounds were particularly problematic for analysis, reporting relative OEU outside of the general trend. This was the case for the heaviest and lightest compounds, the worse separated and the more reactive, in particular for the trimethyl benzene, m,p- xylene, ethyl-benzene, benzene, 1-pentene, 1,3 butadiene and isoprene.

References

1) Directive 2008/50/EC of the European parliament and of the council of 21 May 2008 on ambient air quality and cleaner air for Europe. OJ L152/1 of 11.6.2008

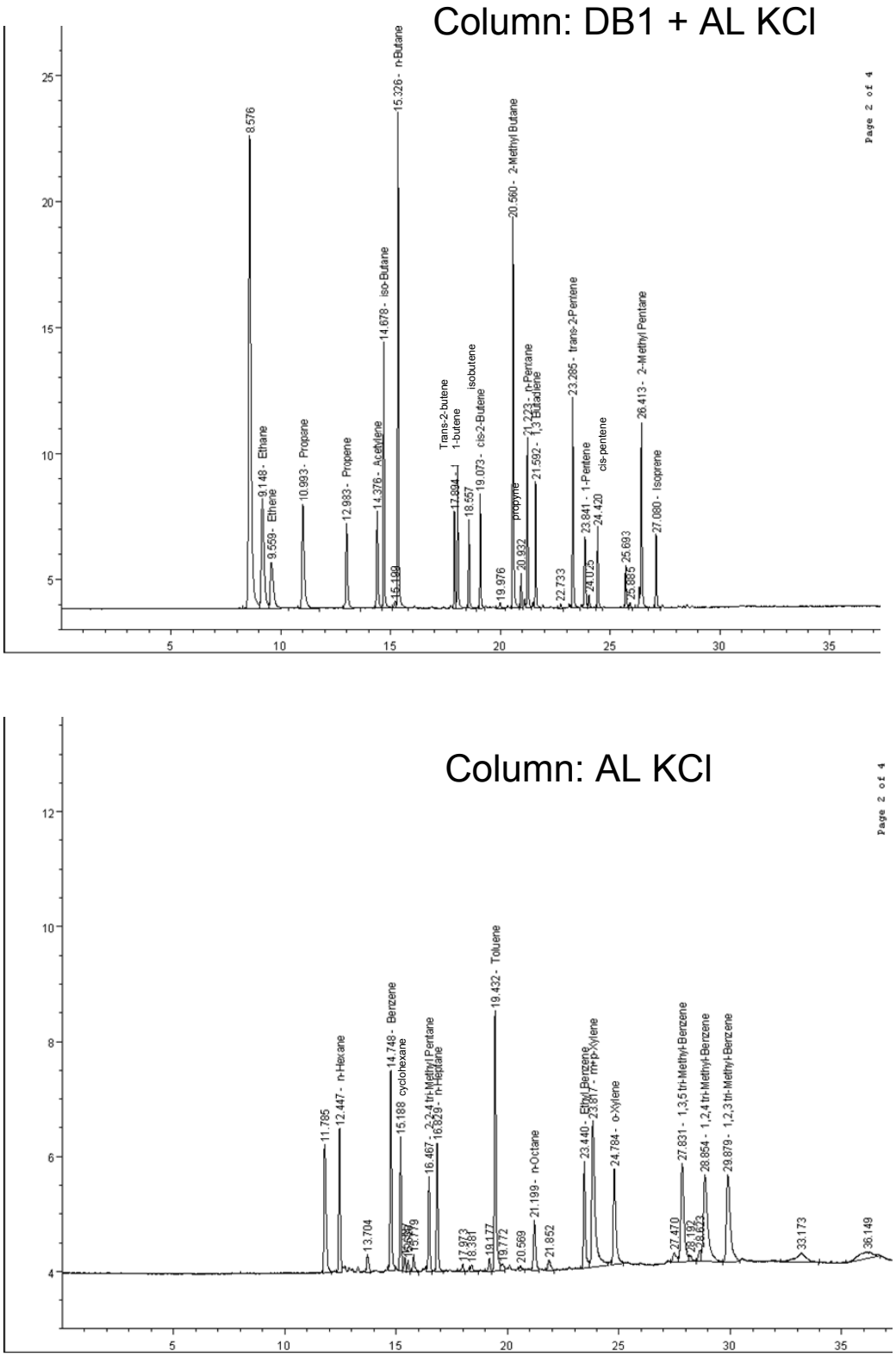
2) EUROMET 886: http://www.euromet.org/

3) ISO 13528: 2005. Statistical methods for use in proficiency testing by interlaboratory comparison.

4) ISO Guide 43-1: 1997. Proficiency testing by interlaboratory comparisons- Part 1 Development and operation of proficiency testing.

Annex I

- Chromatographic separation of the ambient air mixture



Chromatogram of the Ambient air mixture cylinder analysed with a double column (dean switch system): DB1 + AL ClK columns of 50 m and 0.32 mm i.d.

Annex II

- Method description provided by the participating laboratories

Method description

AEAT

INSTRUMENTATION	trade mark	model
Desorption system	Perkin Elmer Turbomatrix	300TD
Gas chromatograph	Perkin Elmer Clarus	500GC
mass spectrometer		

SAMPLING

	Heating Temperature, °C
Transfer Line	200
needle valve	

	from, bar	to, bar
pressure reduction		

sampling temperature, °C	-30
sampling flow, ml/min	20
vent flow, ml/min	0.5
sampling time, s	2400
Sampling volume, ml	800
Drier	Nafion
Adsorbent	Carbotrap B, Carbosieve SIII
amount of adsorbent, mg	65

DESORPTION

desorption flow, ml/min	
desorption temperature, °C	300
desorption time, s	60

CLEANING

backflush flow, ml/min	
backlush temperature, °C	
backflush time, s	

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm
cryotrap description			
cooling system			

cryotrap LOW temperature, °C	
cryotrap HIGH temperature, °C	
transfer line temperature, °C	

MS ACQUISITION PARAMETERS

MS Quad temperature, C		
MS Source temperature, C		
Adquisition mode	Scan	
	SIM	

Solvent delay, min
EM Offset
Resulting EM Voltage

SCAN, especify parameters
SIM, define GROUPS, Plot ions and Qualifiers

GC conditions

carrier gas	Helium
Carrier gas flow, ml/min	4
Hydrogen flow, ml/min	45
make up flow, ml/min	0
Air flow, ml/min	450

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1	Varian		PLOT-NA2SO3		50	0.32	1
2	SGE		BP1		50	0.22	1

Dean switch system

	1st Column	2nd Column
length, m		
i.d. mm		
flow ml/min		
detector		
carrier gas		
oven temperature, °C		
restrictor diameter		
Equivalent restrictor diameter, mm		
equivalent restrictor length, m		

TEMPERATURE PROGRAM

Additional information

Method description

AOL-UUW

INSTRUMENTATION	trade mark	model
Desorption system	Perkin Elmer	Turbomatrix ATD
Gas chromatograph	Agilent	HP 6890 Series GC-System
mass spectrometer	Agilent	HP 6890 Series MSD

SAMPLING

	Heating Temperature, °C
Transfer Line	
needle valve	

	from, bar	to, bar
pressure reduction	bottle pressure	ca. 1 bar

sampling temperature, °C	25
sampling flow, ml/min	10,6 ml/min
vent flow, ml/min	
sampling time, s	2664
Sampling volume, ml	470
Drier	no
Adsorbent	Air Toxics-Fa. Supelco Cat. Nr.: 25051
amount of adsorbent, mg	ca. 250

DESORPTION

desorption flow, ml/min	50
desorption temperature, °C	325
desorption time, s	300

CLEANING

backflush flow, ml/min	
backlush temperature, °C	
backflush time, s	

FOCCUSING and INJECTION

Perkin Elmer Air Monitoring Trap M 0413628

	brand	i.d. mm	layer thickness, µm
cryotrap description			
cooling system	Peltier		
cryotrap LOW temperature, °C	-40		
cryotrap HIGH temperature, °C	300		
transfer line temperature, °C	200		

GC conditions

carrier gas	Helium
Carrier gas flow, ml/min	*
Hydrogen flow, ml/min	no
make up flow, ml/min	no
Air flow, ml/min	no

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1	Supelco	24256	SPB 624		60	0.25	1.4
2							

Dean switch system

	1st Column	2nd Column
length, m		
i.d. mm		
flow ml/min		
detector		
carrier gas		
oven temperature, °C		
restrictor diameter		
Equivalent restrictor diameter, mm		
equivalent restrictor length, m		

TEMPERATURE PROGRAM Initial 33 °C / 6°C/min-->150 °C / 10°C/min --> 250°C / 5 min

Additional information

*Thermodesorber-Flows:	Desorb : 50 ml/min
	Inlet split : off
	Outlet Split : 9 ml/min

Method description

CHMI

INSTRUMENTATION	trade mark	model
Desorption system	Entech Instruments	7100
Gas chromatograph	Agilent (HP) 6890	G1530A
mass spectrometer		

SAMPLING

	Heating Temperature, °C	
Transfer Line	100	
needle valve	100	
	from, bar	**to, bar**
pressure reduction		
sampling temperature, °C	-150	
sampling flow, ml/min	150	
vent flow, ml/min		
sampling time, s		
Sampling volume, ml	100	
Drier	Silica	
Adsorbent	M1 sorbent	
amount of adsorbent, mg	200	

DESORPTION M1

desorption flow, ml/min	10
desorption temperature, °C	180
desorption time, s	240

CLEANING

backflush flow, ml/min	40
backlush temperature, °C	185
backflush time, s	200

FOCCUSING and INJECTION M2

	brand	i.d. mm	layer thickness, µm
cryotrap description	Tenax	2	
cooling system			
cryotrap LOW temperature, °C	-60		
cryotrap HIGH temperature, °C	180		
transfer line temperature, °C	100		

MS ACQUISITION PARAMETERS

MS Quad temperature, C		
MS Source temperature, C		
Adquisition mode	Scan	
	SIM	

Solvent delay, min
EM Offset
Resulting EM Voltage

SCAN, especify parameters
SIM, define GROUPS, Plot ions and Qualifiers

GC conditions

carrier gas	Helium
Carrier gas flow, ml/min	4
Hydrogen flow, ml/min	30
make up flow, ml/min	30
Air flow, ml/min	300

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1	DB1 (ethane-isoprene)				60	0.32	1.0
2	PLOT Al2O3 (hept-123tMbnz)				50	0.32	8.0

Dean switch system

	1st Column	2nd Column
length, m		
i.d. mm		
flow ml/min		
detector		
carrier gas		
oven temperature, °C		
restrictor diameter		
Equivalent restrictor diameter, mm		
equivalent restrictor length, m		

TEMPERATURE PROGRAM 50-218-200-3

Additional information

Method description

CNR

INSTRUMENTATION	trade mark	model
Desorption system	Preconcentratore Entech	7100A
Gas chromatograph / FID	Thermo	Trace GC Ultra

SAMPLING

	Heating Temperature, °C	
Transfer Line	100	
needle valve		
	from, bar	**to, bar**
pressure reduction	0.27	2.07
sampling temperature, °C	-100	
sampling flow, ml/min	100	
vent flow, ml/min		
sampling time, s	240/1800	
Sampling volume, ml	400/2000	
Drier		
Adsorbent	Tenax	
amount of adsorbent, mg		

DESORPTION

desorption flow, ml/min	100
desorption temperature, °C	180
desorption time, s	120

CLEANING

backflush flow, ml/min	100
backlush temperature, °C	190
backflush time, s	180

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm
cryotrap description	Entech	0.5	
cooling system	Liquid Nitrogen		
cryotrap LOW temperature, °C	-150		
cryotrap HIGH temperature, °C	90		
transfer line temperature, °C	100		

MS ACQUISITION PARAMETERS

MS Quad temperature, C		
MS Source temperature, C	200	
Adquisition mode	Scan	**X**
	SIM	
Solvent delay, min	1	
EM Offset		
Resulting EM Voltage	3000	
SCAN, especify parameters	20-350 amu	
SIM, define GROUPS, Plot ions and Qualifiers		

GC conditions

carrier gas	helium
Carrier gas flow, ml/min	5-2,6
Carrier gas Pressure /Kpa	50KPa
Hydrogen flow, ml/min	35
make up flow, ml/min	30
Air flow, ml/min	350

Column

	brand	Code	name	phase	length, m	id. mm
1	Chrompack	7568	Plot fused silica	AL_2O_3/NA_2SO_4	50	0.53
2						

Dean switch system

	1st Column	2nd Column
length, m		
i.d. mm		
flow ml/min		
detector		
carrier gas		
oven temperature, °C		
restrictor diameter		
Equivalent restrictor diameter, mm		
equivalent restrictor length, m		

TEMPERATURE PROGRAM 50°C-3min 5°C/min to 200°C - 20min

Additional information

Method description

CNR-MS

INSTRUMENTATION	trade mark	model
Desorption system	Chrompack	Purge and trap injector
Gas chromatograph	Hewelett Packard	5890
mass spectrometer	Hewelett Packard	5970

SAMPLING

	Heating Temperature, °C	
Transfer Line	Ambient	
needle valve	Ambient	
	from, bar	**to, bar**
pressure reduction	YES	
sampling temperature, °C	Ambient	
sampling flow, ml/min	150	
vent flow, ml/min		
sampling time, s	7	
Sampling volume, ml	1000	
Drier		
Adsorbent	Carbopack C + Carbograph 1 + Carbograph 5	
amount of adsorbent, mg	102mg + 114mg + 224mg	

DESORPTION

desorption flow, ml/min	20
desorption temperature, °C	250
desorption time, s	5

CLEANING

backflush flow, ml/min	100
backlush temperature, °C	350
backflush time, s	20

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm
cryotrap description	Chrompack	0.54	5
cooling system			
cryotrap LOW temperature, °C	-190		
cryotrap HIGH temperature, °C	200		
transfer line temperature, °C	200		

MS ACQUISITION PARAMETERS

MS Quad temperature, C		
MS Source temperature, C	200	
Adquisition mode	**Scan**	**X**
	SIM	
Solvent delay, min	1	
EM Offset		
Resulting EM Voltage	3000	

SCAN, especify parameters 20-350 amu
SIM, define GROUPS, Plot ions and Qualifiers

GC conditions

carrier gas	helium
Carrier gas flow, ml/min	1.5
Hydrogen flow, ml/min	
make up flow, ml/min	
Air flow, ml/min	

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1	**Chrompack**		**Fused silica**	**CPsil5**	**50**	**0.32**	**0.4**
2							

Dean switch system

	1st Column	2nd Column
length, m		
i.d. mm		
flow ml/min		
detector		
carrier gas		
oven temperature, °C		
restrictor diameter		
Equivalent restrictor diameter, mm		
equivalent restrictor length, m		

TEMPERATURE PROGRAM Temp1=5°Cx3min Rate1= 3°C/min to 50°C Rate2= 5°C/min to 250°C x 2min

Additional information

Method description

EARS

INSTRUMENTATION	trade mark	model
Desorption system		
Gas chromatograph	Chromato-sud	airmoVOC C6-C12
mass spectrometer	/	

SAMPLING

	Heating Temperature, °C	
Transfer Line		
needle valve		
	from, bar	**to, bar**
pressure reduction		
sampling temperature, °C	25	
sampling flow, ml/min	45	
vent flow, ml/min		
sampling time, s	1350	
Sampling volume, ml		
Drier		
Adsorbent	Carbotrap, 40 mm	
amount of adsorbent, mg		

DESORPTION

desorption flow, ml/min	
desorption temperature, °C	220
desorption time, s	120

CLEANING

backflush flow, ml/min	
backlush temperature, °C	
backflush time, s	

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm
cryotrap description			
cooling system			
cryotrap LOW temperature, °C			
cryotrap HIGH temperature, °C			
transfer line temperature, °C			

MS ACQUISITION PARAMETERS

MS Quad temperature, C		
MS Source temperature, C		
Adquisition mode	Scan	
	SIM	

Solvent delay, min
EM Offset
Resulting EM Voltage

SCAN, especify parameters
SIM, define GROUPS, Plot ions and Qualifiers

GC conditions

carrier gas	H2
Carrier gas flow, ml/min	0.5
Hydrogen flow, ml/min	27
make up flow, ml/min	
Air flow, ml/min	180

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1				DB 2,5	8	0.2	1
2							

Dean switch system

	1st Column	2nd Column
length, m		
i.d. mm		
flow ml/min		
detector		
carrier gas		
oven temperature, °C		
restrictor diameter		
Equivalent restrictor diameter, mm		
equivalent restrictor length, m		

TEMPERATURE PROGRAM

duration	gradient	temperature
60	2	40
300	2	50
180	10	80
460	15	195

Additional information

Method description

EMD

INSTRUMENTATION	trade mark	model
Desorption system	CHROMPACK	AUTO TCT INJECTOR
Gas chromatograph	CHROMPACK	CP 9001

SAMPLING

	Heating Temperature, °C
Transfer Line	ambient
needle valve	

	from, bar	to, bar
pressure reduction		Patm
sampling temperature, °C	-20	
sampling flow, ml/min	36	
vent flow, ml/min	20	
sampling time, s	600	
Sampling volume, ml	360	
Drier	Nafion drier	
Adsorbent	CarbotrapC + Carbotrap B + Carbosieve SIII	
amount of adsorbent, mg	300	

DESORPTION

desorption flow, ml/min	8
desorption temperature, °C	200
desorption time, s	300

CLEANING

backflush flow, ml/min	5.5
backlush temperature, °C	220
backflush time, s	600

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm
cryotrap description	glass beads	0.53	
cooling system	liquid nitrogen		
cryotrap LOW temperature, °C	-180		
cryotrap HIGH temperature, °C	200		
transfer line temperature, °C			

MS ACQUISITION PARAMETERS

MS Quad temperature, C		
MS Source temperature, C		
Adquisition mode	Scan	
	SIM	

Solvent delay, min
EM Offset
Resulting EM Voltage

SCAN, especify parameters
SIM, define GROUPS, Plot ions and Qualifiers

GC conditions

carrier gas	He
Carrier gas flow, ml/min	3
Hydrogen flow, ml/min	30
make up flow, ml/min	30
Air flow, ml/min	250

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1	PLOT Al2O3/KCl				25	0.32	5
2	CP Sil 5CB, low Blead MS				50	0.32	1.2

Dean switch system

	1st Column	2nd Column
length, m	50	25
i.d. mm	0.32	0.32
flow ml/min	2.6	2.8
detector	FID	FID
carrier gas	He	He
oven temperature, °C	35	35
restrictor diameter		
Equivalent restrictor diameter, mm		
equivalent restrictor length, m		

TEMPERATURE PROGRAM 35°C(8min), 3°C/min (145°C), 10°C/min (200°C), 200° (5min)

Additional information

Method description

EMPA

INSTRUMENTATION	trade mark	model
Desorption system	PerkinElmer	TurboMatrix
Gas chromatograph	HP FID	6890
mass spectrometer	-	

SAMPLING

	Heating Temperature, °C	
Transfer Line	60	
needle valve	60	
	from, bar	**to, bar**
pressure reduction	-	-
sampling temperature, °C	-30	
sampling flow, ml/min	20	
vent flow, ml/min	0	
sampling time, s	900	
Sampling volume, ml	300	
Drier	Nafion	
Adsorbent	PerkinElmer Prod Nr. M0413628	
amount of adsorbent, mg	-	

DESORPTION

desorption flow, ml/min	25
desorption temperature, °C	260
desorption time, s	180

CLEANING

backflush flow, ml/min	-
backlush temperature, °C	-
backflush time, s	-

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm
cryotrap description			
cooling system	no secondary trap		
cryotrap LOW temperature, °C			
cryotrap HIGH temperature, °C			
transfer line temperature, °C	200		

MS ACQUISITION PARAMETERS

MS Quad temperature, C		
MS Source temperature, C		
Adquisition mode	Scan	
	SIM	

Solvent delay, min
EM Offset
Resulting EM Voltage

SCAN, especify parameters
SIM, define GROUPS, Plot ions and Qualifiers

GC conditions

carrier gas	Helium
Carrier gas flow, ml/min	25
Hydrogen flow, ml/min	40
make up flow, ml/min	20
Air flow, ml/min	280

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1	VARIAN	CP7518	PLOT	AL2O3/KCL	50	0.53	
2							

Dean switch system

	1st Column	2nd Column
length, m		
i.d. mm		
flow ml/min		
detector		
carrier gas		
oven temperature, °C		
restrictor diameter		
Equivalent restrictor diameter, mm		
equivalent restrictor length, m		

TEMPERATURE PROGRAM initial: 37°C for 9 min, then 6.5°/min to 180 °C, then 50°/min to 200, for 20 min

Additional information

Method description

EPA

INSTRUMENTATION	trade mark	model
Desorption system		
Gas chromatograph	Syntech	GC855
mass spectrometer		

SAMPLING

	Heating Temperature, °C
Transfer Line	
needle valve	

	from, bar	to, bar
pressure reduction		
sampling temperature, °C		
sampling flow, ml/min		
vent flow, ml/min		
sampling time, s		
Sampling volume, ml		
Drier		
Adsorbent		
amount of adsorbent, mg		

DESORPTION

desorption flow, ml/min	
desorption temperature, °C	
desorption time, s	

CLEANING

backflush flow, ml/min	
backlush temperature, °C	
backflush time, s	

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm
cryotrap description			
cooling system			
cryotrap LOW temperature, °C			
cryotrap HIGH temperature, °C			
transfer line temperature, °C			

MS ACQUISITION PARAMETERS

MS Quad temperature, C		
MS Source temperature, C		
Adquisition mode	Scan	
	SIM	

Solvent delay, min
EM Offset
Resulting EM Voltage

SCAN, especify parameters
SIM, define GROUPS, Plot ions and Qualifiers

GC conditions

carrier gas	N2
Carrier gas flow, ml/min	1.5
Hydrogen flow, ml/min	
make up flow, ml/min	
Air flow, ml/min	

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1							
2							

Dean switch system

	1st Column	2nd Column
length, m		
i.d. mm		
flow ml/min		
detector		
carrier gas		
oven temperature, °C		
restrictor diameter		
Equivalent restrictor diameter, mm		
equivalent restrictor length, m		

TEMPERATURE PROGRAM	50 deg C 0-6min, 80 deg c 14-17 min, 50 deg C

Additional information

Automatic GC with PID

Method description

ERLAP

INSTRUMENTATION	trade mark	model
Desorption system	Perkin Elmer	TurboMatrix ATD
Gas chromatograph	Agilent	#
mass spectrometer		

SAMPLING

	Heating Temperature, °C
Transfer Line	250
needle valve	200

	from, bar	to, bar
pressure reduction	80	1.2
sampling temperature, °C	-30	
sampling flow, ml/min	30	
vent flow, ml/min		
sampling time, s	13.3	
Sampling volume, ml	400	
Drier	Nafion	
Adsorbent	Air Monitoring Trap (grafitized carbon black + carbon molecular sieve)	
amount of adsorbent, mg	150	

DESORPTION

desorption flow, ml/min	20
desorption temperature, °C	200
desorption time, s	

CLEANING

backflush flow, ml/min	
backlush temperature, °C	
backflush time, s	

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm
cryotrap description	PE		
cooling system	Peltier		

cryotrap LOW temperature, °C	-30
cryotrap HIGH temperature, °C	250
transfer line temperature, °C	250

GC conditions

carrier gas	Helium
Carrier gas flow, ml/min	1.75
Hydrogen flow, ml/min	40
make up flow, ml/min	40
Air flow, ml/min	450

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1	J&W Scientific	123-105C	DB-1		50	0.32	1.2
2	J&W Scientific	19091P	HP-AL/KCL		50	0.32	8

Dean switch system

	1st Column	2nd Column
length, m	50	50
i.d. mm	0.32	0.32
flow ml/min	5.05	4.45
detector	FID	FID
carrier gas	Helium	Helium
oven temperature, °C	40 - 200	40 - 200
restrictor diameter	0.1	0.1
Equivalent restrictor diameter, mm	0.25	0.25
equivalent restrictor length, m	1	1

TEMPERATURE PROGRAM h; 6°C/min, 200°C hold 15min

Additional information

Calculation results	1st column	2nd column
Inlet presure	24.69	22.4
Avg. linear velocity cm/s	7.65	43.06
hold up time, min	10.9	1.935
Restrictor length, m		0.477
" hold up time, min		0.002

Caculation inputs	1st column	2nd column
length, m	50	50
i.d., mm	0.32	0.32
flow, ml/min	0.9	3.6
detector	FID	FID
detector pressure,abs	14.7	14.7
carrier gas		helium
pressure units		psi
oven temperature		40
restrictor diameter		0.1
equivalent restrictor diameter, mm		0.25
equivalent restrictor length, m		1

Method description

FMI

INSTRUMENTATION	trade mark	model
Desorption system		
Gas chromatograph	Agilent 6890/FID	
mass spectrometer		

SAMPLING

	Heating Temperature, °C
Transfer Line	
needle valve	

	from, bar	to, bar
pressure reduction		
sampling temperature, °C		
sampling flow, ml/min		
vent flow, ml/min		
sampling time, s		
Sampling volume, ml	300 ml	
Drier	K2CO3	
Adsorbent		
amount of adsorbent, mg		

DESORPTION

desorption flow, ml/min	
desorption temperature, °C	
desorption time, s	

CLEANING

backflush flow, ml/min	
backlush temperature, °C	
backflush time, s	

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm
cryotrap description			
cooling system			
cryotrap LOW temperature, °C			
cryotrap HIGH temperature, °C			
transfer line temperature, °C			

MS ACQUISITION PARAMETERS

MS Quad temperature, C		
MS Source temperature, C		
Adquisition mode	Scan	
	SIM	

Solvent delay, min
EM Offset
Resulting EM Voltage

SCAN, especify parameters
SIM, define GROUPS, Plot ions and Qualifiers

GC conditions

carrier gas	He
Carrier gas flow, ml/min	2.77
Hydrogen flow, ml/min	31.4
make up flow, ml/min	45
Air flow, ml/min	277

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1	Chrompack	Al2O3/KCl PLOT			50	0.32	5
2							

Dean switch system

	1st Column	2nd Column
length, m		
i.d. mm		
flow ml/min		
detector		
carrier gas		
oven temperature, °C		
restrictor diameter		
Equivalent restrictor diameter, mm		
equivalent restrictor length, m		

TEMPERATURE PROGRAM

Additional information

The air samples are collected into evacuated stainless steel canisters (0.85 l) using a Teflon membrane pump.
Prior to analysis, samples are passed through a stainless steel tube (10cm* 1/4'')
filled with K2CO3 and NaOH in order to dry them. Air samples are concentrated in two liquid nitrogen traps.
The first trap is a stainless steel loop (1/8''*125cm) filled with glass beads, while the other one is a capillary trap.

Method description

FMI-MS

INSTRUMENTATION	trade mark
Desorption system	Perkin-Elmer Turbo Matrix 650
Gas chromatograph	Hewlett-Packard 5890 series 2
mass spectrometer	Hewlett-Packard 5972

SAMPLING pumped sampling on adsorbent tubes

	Heating Temperature, °C
Transfer Line	200
needle valve	

	from, bar	to, bar
pressure reduction		
sampling temperature, °C	room temperature	
sampling flow, ml/min	100 ml/min	
vent flow, ml/min		
sampling time, s	5 min	
Sampling volume, ml	500 ml	
Drier		
Adsorbent	Tenax-TA-Carbopack-B	
amount of adsorbent, mg		

DESORPTION

desorption flow, ml/min	50 ml/min
desorption temperature, °C	300
desorption time, s	300

CLEANING

backflush flow, ml/min	
backlush temperature, °C	
backflush time, s	

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm
cryotrap description	Tenax		
cooling system	peltier element		
cryotrap LOW temperature, °C	-30		
cryotrap HIGH temperature, °C	300		
transfer line temperature, °C	200		

MS ACQUISITION PARAMETERS

MS Quad temperature, C	150	
MS Source temperature, C		
Adquisition mode	SIM	
Solvent delay, min	5	
EM Offset		
Resulting EM Voltage		

SCAN, especify parameters
SIM, define GROUPS, Plot ions and Qualifiers
Masses detected are on a result sheet

GC conditions

carrier gas	He
Carrier gas flow, ml/min	1 ml/min
Hydrogen flow, ml/min	
make up flow, ml/min	
Air flow, ml/min	

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1		CP Sil-5 CB			60	0.25	1
2							

Dean switch system

	1st Column	2nd Column
length, m		
i.d. mm		
flow ml/min		
detector		
carrier gas		
oven temperature, °C		
restrictor diameter		
Equivalent restrictor diameter, mm		
equivalent restrictor length, m		

			rate (C/min)	
TEMPERATURE PROGRAM	stage 1	50 C-150 C	4	
	stage 2	150 C-250 C	8	hold 5 min at 250 C

Additional information

Method description

ISSeP

INSTRUMENTATION	trade mark	model
Desorption system	Turbomatrix Thermodesorber	Perkin Elmer
Gas chromatograph	Clarus 500 GC	Perkin Elmer
mass spectrometer	Clarus 500 MS	Perkin Elmer

SAMPLING

	Heating Temperature, °C
Transfer Line	
needle valve	

	from, bar	to, bar
pressure reduction		1

sampling temperature, °C	22
sampling flow, ml/min	20
vent flow, ml/min	0
sampling time, s	10800
Sampling volume, ml	3600
Drier	none
Adsorbent	Carbopack B, Carbopack C, Carbosieve III
amount of adsorbent, mg	475

DESORPTION

desorption flow, ml/min	80
desorption temperature, °C	350
desorption time, s	240

CLEANING

backflush flow, ml/min	-
backlush temperature, °C	-
backflush time, s	-

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm
cryotrap description			
cooling system			
cryotrap LOW temperature, °C	-30		
cryotrap HIGH temperature, °C	300		
transfer line temperature, °C	250		

MS ACQUISITION PARAMETERS

MS Quad temperature, C		
MS Source temperature, C	180	
Adquisition mode	Scan	X
	SIM	
Solvent delay, min	5	
EM Offset		
Resulting EM Voltage		

SCAN, especify parameters 35 to 350 µma
SIM, define GROUPS, Plot ions and Qualifiers

GC conditions

carrier gas	He	
Carrier gas flow, ml/min	1.6	(initial flow)
Hydrogen flow, ml/min		
make up flow, ml/min		
Air flow, ml/min		

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1	JW scientific	123-1364	DB -624		60	0.32	1.8
2				6% cyanopropylphenyl - 94% diméthyl polysiloxane			

Dean switch system

	1st Column	2nd Column
length, m		
i.d. mm		
flow ml/min		
detector		
carrier gas		
oven temperature, °C		
restrictor diameter		
Equivalent restrictor diameter, mm		
equivalent restrictor length, m		

TEMPERATURE PROGRAM 35 °C for 5 min; rate of 3°C/min to 50°C; rate of 6°C/min to 110°C; rate of 10°C/min to 245°C; hold time : 5 min

Additional information

cryotrap description : air monitoring trap from Perkin Elmer - I have no more information
sampling : different sampling volumes and sampling methods was used (direct deposit on tube from the gas cylinder or use of a Tedlar Bag and a sampling pump : more real conditions).
The values in the table are one of them
Adsorbent : amount of each adsorbent are respectively 230mg, 150 mg and 95 mg

Method description

IVL

INSTRUMENTATION	trade mark	model
Desorption system	Markes	Unity + AirServer
Gas chromatograph	Varian	Varian 3800

SAMPLING

	Heating Temperature, °C
Transfer Line	140
needle valve	140

	from, bar	to, bar
pressure reduction		

sampling temperature, °C	-10
sampling flow, ml/min	12
vent flow, ml/min	
sampling time, s	2400
Sampling volume, ml	474
Drier	Nafion drier
Adsorbent	Directly on Water Management Trap from Markes
amount of adsorbent, mg	

DESORPTION

desorption flow, ml/min	
desorption temperature, °C	
desorption time, s	

CLEANING

backflush flow, ml/min	16
backlush temperature, °C	-10
backflush time, s	480

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm
cryotrap description	Markes		
cooling system			
cryotrap LOW temperature, °C	-10		
cryotrap HIGH temperature, °C	300		
transfer line temperature, °C	140		

MS ACQUISITION PARAMETERS

MS Quad temperature, C		
MS Source temperature, C		
Adquisition mode	Scan	
	SIM	

Solvent delay, min
EM Offset
Resulting EM Voltage

SCAN, especify parameters
SIM, define GROUPS, Plot ions and Qualifiers

GC conditions

carrier gas	He
Carrier gas flow, ml/min	1
Hydrogen flow, ml/min	32
make up flow, ml/min	25
Air flow, ml/min	300

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1	Chrompack	CP8780	CP-Sil 5 CB		60	0.25	1.0
2	Chrompack	CP7565	Plot Al2O3/NaSO4		50	0.32	5.0

Dean switch system

	1st Column	2nd Column
length, m	60	50
i.d. mm	0.25	0.32
flow ml/min		
detector	FID	FID
carrier gas	He	He
oven temperature, °C	column oven	column oven
restrictor diameter		
Equivalent restrictor diameter, mm	0.25	
equivalent restrictor length, m	25	

TEMPERATURE PROGRAM 35^0C for 5 min, 3^0C/min to 100^0C. 13^0C/min to 140^0C. 25^0C/min to200^0C.

Additional information

Method description

NPL

INSTRUMENTATION	trade mark	model
Desorption system	Varian sample preconcentration trap	Short Glass Beads
Gas chromatograph	Varian 3600 CX	
mass spectrometer		

SAMPLING

	Heating Temperature, °C
Transfer Line	not heated
needle valve	not heated

	from, bar	to, bar
pressure reduction	n/a	

sampling temperature, °C	-165
sampling flow, ml/min	50
vent flow, ml/min	n/a
sampling time, s	120
Sampling volume, ml	100
Drier	n/a
Adsorbent	Glass Beads
amount of adsorbent, mg	unknown

DESORPTION

desorption flow, ml/min	6
desorption temperature, °C	190
desorption time, s	Isothermal

CLEANING

backflush flow, ml/min	n/a
backlush temperature, °C	n/a
backflush time, s	n/a

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm
cryotrap description	n/a		
cooling system			

cryotrap LOW temperature, °C	n/a
cryotrap HIGH temperature, °C	n/a
transfer line temperature, °C	unheated

MS ACQUISITION PARAMETERS

MS Quad temperature, C		
MS Source temperature, C		
Adquisition mode	Scan	
	SIM	

Solvent delay, min
EM Offset
Resulting EM Voltage

SCAN, especify parameters
SIM, define GROUPS, Plot ions and Qualifiers

GC conditions

carrier gas	Helium
Carrier gas flow, ml/min	6
Hydrogen flow, ml/min	30
make up flow, ml/min	30
Air flow, ml/min	300

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1	Varian		PLOT Al2O3	Al2O3/KCl	50	0.53	
2							

Dean switch system

	1st Column	2nd Column
length, m		
i.d. mm		
flow ml/min		
detector		
carrier gas		
oven temperature, °C		
restrictor diameter		
Equivalent restrictor diameter, mm		
equivalent restrictor length, m		

TEMPERATURE PROGRAM

Additional information

Method description

UBA

INSTRUMENTATION	trade mark	model
Desorption system		
Gas chromatograph	AIRMOVOC C2 - C6, AIRMOVOC C6 - C12	# 5821204 (C2 - C6), #2811204 (C6 - C12)
mass spectrometer	no	no

GC/FID for automatic monitoring of VOC in air (field instrument, 1 measurement every 30 min)

SAMPLING

	Heating Temperature, °C
Transfer Line *	ambient
needle valve	- -

	from, bar	to, bar
pressure reduction	delta p = 0	

sampling temperature, °C	ambient
sampling flow, ml/min	C2 - C6: 13ml/min; C6 - C12: 16 ml/min
vent flow, ml/min	- -
sampling time, s	600
Sampling volume, ml	C2 - C6: 130 ml; C6 - C12: 160 ml
Drier	typ: PermaPure (C2 - C6)
Adsorbent	C2 - C6: airmoSORB VOC (Carbotrap/Carbosieve/Carboxen
	C6 - C12: airmoSORB VOC (Monophase: CarbotrapC)
amount of adsorbent, mg	C2 - C6: 1,5 cm/phase, 1mm id.; C6 - C12: 6 cm, 1 mm id.

V bypass: 3l/h

DESORPTION

desorption flow, ml/min	C2 - C6: 8-9 ml/min; C6 - C12: 6 ml/min
desorption temperature, °C	C2 - C6: 360°C; C6 - C12: 335°C
desorption time, s	C2 - C6: 180s; C6 - C12: 120s

CLEANING

backflush flow, ml/min	- -
backlush temperature, °C	- -
backflush time, s	- -

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm
cryotrap description	- -	- -	- -
cooling system			
cryotrap LOW temperature, °C	- -		
cryotrap HIGH temperature, °C	- -		
transfer line temperature, °C	- -		

MS ACQUISITION PARAMETERS	- -	
MS Quad temperature, C	- -	
MS Source temperature, C	- -	
Adquisition mode	Scan	- -
	SIM	- -
Solvent delay, min	- -	
EM Offset	- -	
Resulting EM Voltage	- -	

SCAN, especify parameters	- -	
SIM, define GROUPS, Plot ions and Qualifiers		- -

GC conditions

carrier gas	H2
Carrier gas flow, ml/min	C2 - C6: 8 ml/min; C6 - C12: 6 ml/min (at a temperature of 40°C)
Hydrogen flow, ml/min	- -
make up flow, ml/min	- -
Air flow, ml/min	- -

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1	C2 - C6: PoraplotQ				30	0.53	1.5
2	C6 - C12: WCOT Fused Silica			DB-1	30	0.18	1

Dean switch system

	1st Column	2nd Column
length, m	- -	- -
i.d. mm	- -	- -
flow ml/min	- -	- -
detector	- -	- -
carrier gas	- -	- -
oven temperature, °C	- -	- -
restrictor diameter	- -	- -
Equivalent restrictor diameter, mm	- -	- -
equivalent restrictor length, m	- -	- -

TEMPERATURE PROGRAM C2 - C6: 40°C 60sec isotherm, 40°C - 190°C: 15°C/min, 190°C 360 sec isotherm

C6 - C12: 40°C 60sec isotherm, 40°C - 50°C: 2°C/min, 50°C - 80°C: 10°C/min, 80°C - 195°C: 15°C/min, 195°C: 420sec isotherm

Additional information

* sample gas tube: external: PFA: 4mm id., length 2m (1m drier typ Nafion), synth. air for drying
internal: PFA: 2 mm id., length 50cm, stainless steel capillary: 1 mm id., length 30cm

cooling system C2 - C6: compressed air (Vortex-effect)
detection: FID (C2 - C6, C6 - C12)
flow control: critical orifice

Method description

VMM

INSTRUMENTATION	trade mark	model
Desorption system	Perkin Elmer	TurboMatrix ATD
Gas chromatograph	Perkin Elmer	Autosystem XL
Flam Ionisation Detection	Perkin Elmer	Autosystem XL

SAMPLING

	Heating Temperature, °C	
Transfer Line	/	
needle valve	/	
	from, bar	**to, bar**
pressure reduction		
sampling temperature, °C	ambient	
sampling flow, ml/min	300	
vent flow, ml/min	20	
sampling time, s	1800 s	
Sampling volume, ml	10L	
Drier	none	
Adsorbent	Carbopack C, Carbopack B & Carbosieve III 60/80	
amount of adsorbent, mg	625	

DESORPTION

desorption flow, ml/min	110
desorption temperature, °C	350
desorption time, s	480 s

CLEANING	NA
backflush flow, ml/min	
backlush temperature, °C	
backflush time, s	

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm
cryotrap description	Tenax trap	3.5	2500
cooling system			
cryotrap LOW temperature, °C	-30		
cryotrap HIGH temperature, °C	330		
transfer line temperature, °C	200		

MS ACQUISITION PARAMETERS	NA	
MS Quad temperature, C		
MS Source temperature, C		
Adquisition mode	Scan	
	SIM	

Solvent delay, min
EM Offset
Resulting EM Voltage

SCAN, especify parameters
SIM, define GROUPS, Plot ions and Qualifiers

GC conditions

carrier gas	Helium
Carrier gas flow, ml/min	5.35
Hydrogen flow, ml/min	45
make up flow, ml/min	
Air flow, ml/min	450

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1			Chrompack	CPSil5	100	0.53	0.5
2							

Dean switch system NA

	1st Column	2nd Column
length, m		
i.d. mm		
flow ml/min		
detector		
carrier gas		
oven temperature, °C		
restrictor diameter		
Equivalent restrictor diameter, mm		
equivalent restrictor length, m		

TEMPERATURE PROGRAM 0°C (5'), up to 150 °C (4°C/min),
up to 200°C (10 °C/min), 200°C untill end of analysis

Additional information

The method is based on a two-stage desorption. The sample tube is heated for a set period (8' - 350°C) and the volatiles are reconcentrated on the cold trap (-30°C). At the end, the cold trap is heated rapidly (up to 330 °C in 4') to release the volatiles to the GC.
Sample split point after desorption on the inlet of the cold trap. Splitratio: 110/11cc.

Method description

VMM-S1

INSTRUMENTATION	trade mark	model
Desorption system	Synspec	syntech 955
Gas chromatograph	Synspec	GC 955 GC1
mass spectrometer	detection: Synspec Photo Ionisation Detector	build in syntech 955 GC 1

SAMPLING

	Heating Temperature, °C	
Transfer Line	/	
needle valve	/	
	from, bar	**to, bar**
pressure reduction		
sampling temperature, °C	ambient	
sampling flow, ml/min	30	
vent flow, ml/min	3	
sampling time, s	1680	
Sampling volume, ml	315	
Drier	Perma Pur based on Nafion	
Adsorbent	directly preconcentrated on tenax	
amount of adsorbent, mg		

DESORPTION no external desorptionsystem

desorption flow, ml/min	/
desorption temperature, °C	/
desorption time, s	/

CLEANING

backflush flow, ml/min	1.5
backlush temperature, °C	64
backflush time, s	120

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm	
cryotrap description	Tenax GR35-60mesh			
cooling system	none			
cryotrap LOW temperature, °C		45		depends on internal T of the instrument
cryotrap HIGH temperature, °C		190		
transfer line temperature, °C	none			

MS ACQUISITION PARAMETERS

MS Quad temperature, C		
MS Source temperature, C		
Adquisition mode	Scan	
	SIM	

Solvent delay, min
EM Offset
Resulting EM Voltage

SCAN, especify parameters
SIM, define GROUPS, Plot ions and Qualifiers

GC conditions

carrier gas	nitrogen	
Carrier gas flow, ml/min	Flowprogram:	start:1.5 cc
		end: 3.0 cc
Hydrogen flow, ml/min		flowrampstart on 3.3 min
make up flow, ml/min		flowrampend on 10 min
Air flow, ml/min		

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1	synspec	AT624	stripper	95% dimethylpolysiloxane,	2	0.32	1.8
2	synspec	AT624	analysis	95% dimethylpolysiloxane,	28	0.32	1.8

Dean switch system not used

	1st Column	2nd Column
length, m		
i.d. mm		
flow ml/min		
detector		
carrier gas		
oven temperature, °C		
restrictor diameter		
Equivalent restrictor diameter, mm		
equivalent restrictor length, m		

TEMPERATURE PROGRAM 0 - 3': 64°C; 3 - 7': up to 95°C; 7' - end of cycle: 95°C

Additional information

The GC955 works continuously: while analysing, the following 'half an hour' sample is preconcentrated on the trap.
After the nafiondrier the sample gas line divides into 2 separate lines. One is connected with the GC1,
it has only a PID and is fit to measure C6-C10 compounds. The other connects the GC2 that includes
both a PID and an FID in serial combination and measures the compounds with low boiling point < C6.
The conditions and settings of this GC2 are in the next file.

Method description

VMM-S2

INSTRUMENTATION	trade mark	model
Desorption system	Synspec	syntech 955
Gas chromatograph	Synspec	GC 955 GC2
mass spectrometer	detection: Synspec Photo Ionisation + Flame Ionisatio	build in syntech 955 GC2

SAMPLING

	Heating Temperature, °C	
Transfer Line	/	
needle valve	/	
	from, bar	**to, bar**
pressure reduction		
sampling temperature, °C	ambient	
sampling flow, ml/min	30	
vent flow, ml/min	3	
sampling time, s	1680	
Sampling volume, ml	315	
Drier	Perma Pur based on Nafion	
Adsorbent	directly preconcentrated on tenax&carbosive	
amount of adsorbent, mg		

DESORPTION no external desorptionsystem

desorption flow, ml/min	/
desorption temperature, °C	/
desorption time, s	/

CLEANING

backflush flow, ml/min	1.5
backlush temperature, °C	40
backflush time, s	120

FOCCUSING and INJECTION

	brand	i.d. mm	layer thickness, µm
cryotrap description	coold precon with tenax and		carbosive
cooling system	Peltier		
cryotrap LOW temperature, °C	0		
cryotrap HIGH temperature, °C	270		
transfer line temperature, °C	none		

MS ACQUISITION PARAMETERS

MS Quad temperature, C		
MS Source temperature, C		
Adquisition mode	Scan	
	SIM	

Solvent delay, min
EM Offset
Resulting EM Voltage

SCAN, especify parameters
SIM, define GROUPS, Plot ions and Qualifiers

GC conditions

carrier gas	nitrogen	start:1.5 cc
Carrier gas flow, ml/min		end: 4.0 cc
		flowrampstart on 10 min
Hydrogen flow, ml/min	20	flowrampend on 17 min
make up flow, ml/min		
Air flow, ml/min	250	

Column

	brand	Code	name	phase	length, m	id. mm	layer thickness, µm
1	synspec	capillary colun	stripper	95% dimeth	5	0.32	1
2	synspec	Plot column	analysis	Al2O3/Na2	10		

Dean switch system not used

	1st Column	**2nd Column**
length, m		
i.d. mm		
flow ml/min		
detector		
carrier gas		
oven temperature, °C		
restrictor diameter		
Equivalent restrictor diameter, mm		
equivalent restrictor length, m		

TEMPERATURE PROGRAM 0 - 3': 40°C; 3 - 10': up to 110°C; 7' - end of cycle: 110°C

Additional information

Annex III

- Uncertainty evaluation reported by participating laboratories

example for ETHANE

certificate: ppb 4.03
stdev calibration: 701.7840124 in area units for 5 calibrations
average area calibration: 47959.4 in area units for 5 calibrations
average area blank: 679 in area units for 5 blanks
stdev blank: 342.6504536
response factor ppb/area: 8.52362E-05
response factor * stdev calibration: 0.059817378
response factor * stdev blank: 0.057875356
certificate uncertainty: 0.08
k = 2u certificate: 0.04

rf * stdev calibration squared: 0.003578119 (a)
rf * stdev blank squared: 0.003349557 (b)
k squared: 0.0016 (c)

sum uncertainties: 0.008527676 (a+b+c)

square root of sum uncertainties: 0.092345415

expanded uncertainty: 0.184690829

this is recalculated for each compound and used for all measurements.

REFERENCE MATERIAL:

Manufacturer: NPL
certification date: 13/12/2005
Expiry date: information not provided by the laboratory
Pressure of the cylinder: information not provided by the laboratory.

Relative Expanded Uncertainty: ~ ± 2 %
Concentration level: ~ 4 ppb (m/m)
CONSECUTIVE ANALYSIS
1 response factor

Vertrauensbereich des Mittelwertes:

VB=t(alpha,f) * (s/sqr n) alpha=95 % (=2 sigma)

Associated uncertainty = %-Deviation * 1,5 (=Sicherheitsfaktor)

REFERENCE MATERIAL:

Manufacturer: Spectra Gases

Dilution of Reference gas with Zero-Air Conc.-Levels from ca. 12 ppb - ca. 1,5 ppb adsorption on Air-Toxics Tubes Vol. 470 ml

Certification date: 2/2/2007
Expiry date: 2/2/2008
Pressure of the cylinder: 1800 psig

Concentration level: ~ 1000 ppb (m/m)
Relative Expanded Uncertainty: ~ ± 5 %

Average response factor from different concentrations.
CONSECUTIVE ANALYSIS

CARLOS III

The uncertainty considered two components:

Uncertainty of reference material
Uncertainty of repeatability

REFERENCE MATERIAL:

Manufacturer: Praxair
Certification date: not provided by the laboratory
Expiry date: idem.
Pressure of the cylinder: idem

Relative expanded uncertainty: ± 6 %
Concentration level: ~ 50 ppb(m/m), except isoprene, acetylene and 1,3 butadiene with ~ 10 ppb(m/m).

ANALYSED ON DIFERENT DAYS

Two calibration lines with five points between 0 nmol/mol and 50 nmol/mol were used.

The cylinder' gas was sampled by means of a pressure reducer directly connected to the thermal desorption unit and gas chromatograph.

CHMI

The calibration and measurement were carried out by means of a comparison with the working standard - analyzer with traceability to primary reference materials (PRM). The reported uncertainties of measurement are based on standard uncertainties multiplied by a coverage factor k=2, which for a normal distribution corresponds to a coverage probability of approximately 95%.
The standard uncertainty of has been determined in accordance with documents EA4/02 and Qualimetry 11.- Determination of uncertainty of analytical measurement as expanded uncertainty (coverage factor k=2).
The uncertainty was calculated from the distribution of uncertainty resulting from the standard used, the calibration method and the external conditions for calibration.
Uncertainty is calculated as combined uncertainty from type B.
Constituent elements of B are calculated from:
- Certificate of Calibration of Primary reference gas mixture NPL D83 8766 contains 30 hydrocarbons species in nitrogen with nominal concentration 10 nmol/mol
- Reproducibility of the working etalon - chromatography HP6890 model G1530A
- Repeatibility of calibration material and measured material
- Dependence of sample input pressure

Linearity of the working standard (etalon) has been checked by diluting of the primary reference material by static manometric injection into 6 l silcosteel canisters.
Gas chromatograf HP 6890 model G 1530A has been used as the working standard (etalon) in this intercomparison.

Parameter	Unit	Value	Exp.unc.	Std.unc.	□ rel.unc.	Rel.exp.unc.[%]			
			abs.part *x*			rel.part *y*	std.unc. *y*		
PRM D83 8766									
ethane	nmol/mol	**10.53**	**0.21**	0.105	0.009972	1.99			
Traceability of PE-A HP6890 to PRM									
varriety of in sample press.(4.7 IP-000-09)	%	2	0.02	0.01	0.01	2.00			
PE-A abs.& rel.part *x, y* (4.7 IP-000-09)	nmol/mol, %	DPE-A(PRM)	0.04	0.02		4.06	0.0203		
the number of PRM injection and std.unc.of read PE-A		3		0.12502	0.011873	2.37			
The value PE-A for PRM	nmol/mol	10.53	0.39	0.19428		3.69			
calibration factor $f_{cal,PE\text{-}A(PRM)}$ (~ 1)		1	0.0369	0.01845		3.69			
Calibration of gas source or cylinder									
PE-A abs.& rel.part *x, y* (4.7 IP-000-09)	nmol/mol, %	DTL	0.04	0.02		4.06	0.0203		
the number of PRM injection and std.unc.of read PE-A		3		0.07141	0.012209	2.44			
Concentration of gas source or cylinder	nmol/mol	5.85	**0.26**	0.12941		4.42			
ethane		10.53	0.21	4.06	2.03	5.849			
PRM D83 8766		**Concentration**	***U* (k=2)**	**Rel *y* [%]**	Repeab.[%]	Meas.value	u	**U(k=2)**	U [%]
ethane	<- start calc	10.53	0.21	4.06	2.03	5.849	0.1294	0.26	4.44
ethylene (ethene)	macro	10.46	0.21	5.84	2.92	5.764	0.1615	0.33	5.73
propane	Ctrl+a	10.42	0.21	4.94	2.47	5.836	0.1457	0.3	5.14
propene		10.32	0.21	5.8	2.9	5.772	0.1612	0.33	5.72
iso-butane (2-methylpropane)		10.50	0.21	7.56	3.78	7.902	0.2694	0.54	6.83
acetylene (ethyne)		10.45	0.21	3.78	1.89	5.797	0.1236	0.25	4.31
n-butane		10.20	0.20	6.6	3.3	7.647	0.2336	0.47	6.15
trans-2-butene		10.19	0.20	6.46	3.23	7.610	0.2286	0.46	6.04
1-butene		10.04	0.20	6.38	3.19	7.511	0.2239	0.45	5.99
cis-2-butene		10.05	0.20	6.4	3.2	7.503	0.2242	0.45	6.00
i-pentane (2-methylbutane)		10.17	0.20	5.72	2.86	5.236	0.1444	0.29	5.54
n-pentane		10.32	0.21	5.36	2.68	5.379	0.1423	0.29	5.39
1,3-butadiene		10.31	0.21	6.36	3.18	5.737	0.1715	0.35	6.10
trans-2-pentene		9.82	0.20	5.96	2.98	4.984	0.1424	0.29	5.82
1-pentene		10.00	0.20	6.32	3.16	5.076	0.151	0.31	6.11
i-hexane (2-methylpentane)		10.18	0.20	5.46	2.73	5.252	0.1401	0.29	5.52
n-hexane		10.19	0.20	8.92	4.46	5.279	0.2072	0.42	7.96
isoprene (2-methyl-1,3-butadiene)		10.19	0.20	5.94	2.97	5.220	0.1479	0.3	5.75
n-heptane		10.06	0.20	5.46	2.73	5.215	0.1394	0.28	5.37
benzene		10.28	0.21	5.02	2.51	3.740	0.0958	0.2	5.35
2,2,4-trimethylpentane (i-octane)		10.25	0.21	5.6	2.8	5.307	0.1449	0.29	5.46
n-octane		10.16	0.20	5.84	2.92	5.253	0.1471	0.3	5.71
toluene		10.16	0.20	5.02	2.51	3.281	0.0842	0.17	5.18
ethylbenzene		10.50	0.21	5.74	2.87	4.162	0.1159	0.24	5.77
m+p-xylene		20.77	0.42	5.62	2.81	8.256	0.2239	0.45	5.45
o-xylene		10.31	0.21	6.06	3.03	4.090	0.1188	0.24	5.87
1,3,5-trimethylbenzene		10.07	0.20	7.6	3.8	3.955	0.1365	0.28	7.08
1,2,4-trimethylbenzene		10.56	0.21	8.5	4.25	4.132	0.1563	0.32	7.74
1,2,3-trimethylbenzene		9.62	0.19	9.5	4.75	3.769	0.1569	0.32	8.49

REFERENCE MATERIAL:

Manufacturer: NPL
Certification date: 23 March 2006
Expiry date: 23 March 2008
Pressure of the cylinder: 40 ÷ 20 bar, minimum pressure 10 bar

Relative expanded uncertainty: ± 2 %
Concentration level: ~ 10 nmol/mol

ANALYSED ON DIFERENT DAYS

CNR

In this section you should explain in which way you have calculated the associated Uncertainty of your analysis.
The practice used for the calculation of the uncertainty is based on the International Standard ISO 6143.

On the basis of the calibration line obtained from the reference gas mixture:

$$y = b_0 + b_1 x$$

written in the form y =F(x), where:

x = analyte molar fraction, that is the concentration of the analyte;
y = analyte instrumental response, that is the analyte area found by the instrument;
b0 = intercept of the calibration line;
b1 = slope of the calibration line.

For calculation of the uncertainty, the calibration line has to be written in the equivalent form:

$$x = \frac{y - b_0}{b_1} = \frac{y}{b_1} - \frac{b_0}{b_1}$$

which now is in the form x = G(y).

The equation for the calculation of the standard uncertainty of the analyte content is the square root of the following expression (paragraph 5.3, pag. 12 of the International Standard ISO 6143):

$$u^2(x) = \left(\frac{\partial G}{\partial y}\right)^2 u^2(y) + \sum_{j=0}^{N} \left(\frac{\partial G}{\partial b_j}\right)^2 u^2(b_j) + 2\sum_{j=0}^{N-1}\sum_{l=j+1}^{N} \left(\frac{\partial G}{\partial b_j}\right)\left(\frac{\partial G}{\partial b_l}\right) u(b_j, b_l)$$

equation (1)

where:
u(x) = standard uncertainty of the analyte content;
u(y) = standard uncertainty of the response y, expressed such as its standard deviation;
u2(b0) = variance of the intercept b0 of the analysis function;
u2(b1) = variance of the slope b1 of the analysis function;
u(b0,b1) = covariance of the parameters b0 and b1 of the analysis function;
N = numbers of the parameters of the calibration line.

Since in our situation the equation of the calibration line is linear, the parameters that we have to take into account are just the intercept b0 and the slope b1 of the calibration line so N = 1 and the equation (1) turns into:

$$u^2(x) = \left(\frac{\partial G}{\partial y}\right)^2 u^2(y) + \left(\frac{\partial G}{\partial b_0}\right)^2 u^2(b_0) + \left(\frac{\partial G}{\partial b_1}\right)^2 u^2(b_1) + 2\left(\frac{\partial G}{\partial b_0}\right)\left(\frac{\partial G}{\partial b_1}\right) u(b_0, b_1)$$

equation (2)

Carrying out the partial derivatives, the equation (2) turns into:

$$u^2(x) = \left(\frac{1}{b_1}\right)^2 u^2(y) + \left(-\frac{1}{b_1}\right)^2 u^2(b_0) + \left[-\frac{(y-b_0)}{b_1^2}\right]^2 u^2(b_1) + 2\left(-\frac{1}{b_1}\right)\left[-\frac{(y-b_0)}{b_1^2}\right] u(b_0, b_1)$$

equation (3)

For the calculation of u2(b0), u2(b1) and u(b0, b1), we have used these equations (paragraph A.3.1, pg. 18 of the Annex A of the International Standard ISO 6143):

$$u^2(b_j) = \sum_{i=1}^{n} \left(\frac{\partial b_j}{\partial x_i}\right)^2 u^2(x_i) + \sum_{i=1}^{n} \left(\frac{\partial b_j}{\partial y_i}\right)^2 u^2(y_i) + 2\sum_{i=1}^{n-1} \sum_{h=i+1}^{n} \left(\frac{\partial b_j}{\partial x_i}\right)\left(\frac{\partial b_j}{\partial x_h}\right) u(x_i, x_h)$$

equation (4)

$$u(b_j, b_l) = \sum_{i=1}^{n} \left(\frac{\partial b_j}{\partial x_i}\right)\left(\frac{\partial b_l}{\partial x_i}\right) u^2(x_i) + \sum_{i=1}^{n} \left(\frac{\partial b_j}{\partial y_i}\right)\left(\frac{\partial b_l}{\partial y_i}\right) u^2(y_i) +$$

$$+ 2\sum_{i=1}^{n-1} \sum_{h=i+1}^{n} \left[\left(\frac{\partial b_j}{\partial x_i}\right)\left(\frac{\partial b_l}{\partial x_h}\right) + \left(\frac{\partial b_l}{\partial x_h}\right)\left(\frac{\partial b_j}{\partial x_h}\right)\right] u(x_i, x_h)$$

equation (5)

Where n = numbers of the reference gas mixtures.

Since we used just one reference gas mixture n = 1, so the equations (4) and (5) turn into:

$$u^2(b_j) = \sum_{i=1}^{1} \left(\frac{\partial b_j}{\partial x_i}\right)^2 u^2(x_i) + \sum_{i=1}^{1} \left(\frac{\partial b_j}{\partial y_i}\right)^2 u^2(y_i)$$

equation (6)

$$u(b_j, b_l) = \sum_{i=1}^{1} \left(\frac{\partial b_j}{\partial x_i}\right)\left(\frac{\partial b_l}{\partial x_i}\right) u^2(x_i) + \sum_{i=1}^{1} \left(\frac{\partial b_j}{\partial y_i}\right)\left(\frac{\partial b_l}{\partial y_i}\right) u^2(y_i)$$

equation (7)

For the calculation of u2(b0) and u2(b1) we will use the equation (6).

For u2(b0), we have to carry out some partial derivatives, so it's necessary to invert the equation of the calibration

line according to b0, so it turns into: $b_0 = y - b_1 x$

so:

$$u^2(b_0) = (-b_1)^2 u^2(x_1) + (1)^2 u^2(y_1)$$

in which x1 and y1 are respectively the mean concentration of the analyte and the corresponding mean response.

Similarly for u2(b1), we have to carry out some partial derivatives, so it's necessary to invert the equation of the calibration line according to b1, so it turns into:

$$b_1 = \frac{y - b_0}{x} = \frac{y}{x} - \frac{b_0}{x}$$

so:

$$u^2(b_1) = \left[-\frac{(y - b_0)}{x_1^2} \right]^2 u^2(x_1) + \left(\frac{1}{x} \right)^2 u^2(y_1)$$

For the calculation of u(b0, b1), we have to use the equation (7), which turns into:

$$u(b_0, b_1) = (-b_1) \left[-\frac{(y - b_0)}{x_1^2} \right] u^2(x_1) + (1) \left(\frac{1}{x} \right) u^2(y_1)$$

REFERENCE MATERIAL

Manufacturer: SIAD
We performed two calibration curves introducing respectively 4 and 5 measured amounts of standards, (the first between 0 ppb up to 20 ppb, the second between 0 ppb and 4,5 ppb) into the preconcentrator and conducting 5 replicate analyses for each concentration.

Certification date: 6/8/2007
Expiry date: 6/8/2008
Pressure of the cylinder: 150 bar

Relative Expanded Uncertainty: ~ ± 12 %
Concentration level: ~ 50 ppb (m/m)

ANALYSED ON DIFFERENT DAYS
Use of calibration line (7 different levels of concentration).

EARS

No information provided regarding uncertainty calculation.

REFERENCE MATERIAL:

Manufacturer: SIAD
Certification date: 31/3/2006
Expiry date: 21/3/2007
Pressure of the cylinder:100 bar

Standards available only for > C6
Relative Expanded Uncertainty: ~ ± 7.5 %
Concentration level: ~100 ppb (m/m)

CONSECUTIVE ANALYSIS
Response factor: Information not provided

EMD

Methodology for determination of measurement uncertainty: the total uncertainty is based on a calculation of combining the standard uncertainties calculated from all performance characteristics (according to the methodology used in the CEN 14 662-3). The combined uncertainty (uc) is estimated from the following individual contributions:

- uncertainty associated with the calibration method - practical Response Factor using the average area obtained from approximately 7 analysis of the reference cylinder;
- uncertainty of the reference material used;
- uncertainty associated with the linearity -several analysis have been performed at 5 different concentration levels and the largest relative residual from the linear regression function (Xfit) is used to calculate the standard uncertainty due to lack of fit;
- uncertainty associated with the short term drift -as the response factor did not change between all the independent analysis, the reference gas was analysed several times, the uncertainty associated with this deviation was calculated and taken into account;
- uncertainty associated with the memory effect or blank value" of the analyser -after 3 analysis of the reference gas, "zero air" was injected and the concentration obtained allow us to quantify this parameter;
- uncertainty associated with the repeatability of the measurement -the repeatability standard deviation was calculated for each compound at several concentration levels taking into account the variation of the repeatability depending on the concentration.

The expanded uncertainty at the 95% confidence level is obtained by multiplying the combined uncertainty (uc) with a coverage factor of 2.

REFERENCE MATERIAL:

Manufacturer: NPL
Response factors obtained using the average area from approximately 7 analysis.

Certification date: 9/27/2006
Expiry date: 9/27/2008
Pressure of the cylinder: 85 bars

Another cylinder was used to compare the practical response coefficients:
it's a NMi cylinder but the Expanded uncertainty is more significant than for the
NPL cylinder and some compounds are not present. (i.e.: acetylene, 1,2,3-trimethylbenzene)

Relative Expanded Uncertainty: ~ ± 2 %
Concentration level: ~ 4 ppb (m/m)

ANALYSED ON DIFFERENT DAYS
Average response factor from different concentrations.

EMPA

In this section you should explain in which way you have calculated the associated uncertainty to your analysis. The uncertainty was calculated by making 15 independent standard measurements in the 1-10ppb range and calculating the standard deviation for each compound individually. The extended uncertainty is representing 2 x this standard deviation.

REFERENCE MATERIAL:

Manufacturer: NPL
Injection of 300 ml NPL-standard, same as air sampling
Certification date: 26-Apr-06
Expiry date: 26-Apr-08
Pressure of the cylinder: 40 bar
Relative Expanded Uncertainty: ~ ± 2 %
Concentration level: 4 ppb (m/m)

CONSECUTIVE ANALYSIS
1 response factor.

EPA

No data provided by the laboratory about uncertainty calculation.

REFERENCE MATERIAL:
Liquid samples of the compounds injected into a 10L tedlar bag in air.

Relative expanded uncertainty reported between: 3 to 10 % for BTEX and TMB.

ANALYSED ON DIFFERENT DAYS
Use of response factors.

ERLAP

The main source of uncertainties considered were:

- Uncertainty of the reference material, (uRM),
- Uncertainty of the sampling procedure (sampling volume, adsorption in the pipe), (uS) and
- Uncertainty of the calibration procedure (ISO 6143), multi-point calibration, (uCi = f(URM, uS))

The final combined uncertainty was calculated according to the reproducibility uncertainty based on 5 analyses during 5 different days with 5 different calibrations: (uR = SQRT((∑uci^2 + stdv(ci)^2)/5)

Cylinders were kept in the laboratory for at least 2 weeks prior to analysis to reach stable conditions. Cylinders were connected to the instrument for sampling through a 1/8" Teflon tube of about 1 m length. A pressure reducer with a needle valve was used to regulate the inlet flow pressure to about 2 bar. A sampling flow was automatically regulated by the mass flow of the instrument, which was operating at a fixed flow of circa 25 ml/min.

REFERENCE MATERIAL:

Manufacturer: NPL
certification date: 14/09/2006
Expiry date: 13/9/2008
Pressure of the cylinder: 80 bar

Primary reference gas mixture 30 hydrocarbons species (ozone precursors in N2), cylinder n D95 4835.

Relative expanded uncertainty: ± 2.5 %
Concentration level: ~ 4 ppb (m/m)

ANALYSED ON DIFFERENT DAYS
Use of a calibration line:
The sampling volumes for the gravimetric and ambient air sample were 400 and 750 ml, respectively. The calibration line was carried out by varying the sampling time and keeping the flow constant during sampling to cover the concentration level of the cylinders.

FMI

Method I: Canister analysis

The uncertainty of the canister analysis was evaluated from the standard deviation of the analysis of samples from two parallel canisters over a yearly period. This could only be calculated for the compounds that exist in our samples, for the rest of the compounds we used the average of these uncertainties.

	mean standard deviation (%)
ethane	4
ethene	13
propane	5
propene	18
2-methylpropane	12
ethyne	18
butane	14
1-butene	28
2-methylpropene	23
2-methylbutane	15
pentane	12
cyclohexane	11
2-methylpentane	26
3-methylpentane	33
hexane	23
isoprene	32
heptane	28
Average	19

Method II: Adsorbent tubes

The uncertainty of the adsorbent tubes was evaluated using the reference material (BCR CRM112) for benzene, toluene and xylene.

The reference material is not available for the remainder of the compounds. The uncertainties were calculated for the rest of the compounds by considering the uncertainty contribution from sampling, analysis, desorption and calibration.

A more detailed description of the method is described in Hellén H, Hakola H., Laurila T., Hiltunen V. and Koskentalo T., 2002. Aromatic hydrocarbon and methyl tert-butyl ether measurements in Helsinki (Finland) using diffusive samplers. Science of the Total Environment 298, 55-64.

	MU %
Benzene	20
Toluene	20
Ethylbenzene	14
p/m-xylene	26
Styrene	26
o-xylene	13
Propylbenzene	20
3-Ethyltoluene	21
4- Ethyltoluene	23
2- Ethyltoluene	23
1,3,5-trimethylbenzene	20
1,2,4-trimethylbenzene	18
1,2,3-trimethylbenzene	18

REFERENCE MATERIAL

Manufacturer: NPL
Certification date: Nov-05
Expiry date: information not provided by the laboratory
Pressure of the cylinder: 70 bar

Compounds from ethane to heptane has been calibrated using NPL standard.

Aromatic compounds have been calibrated using liquid standards prepared from pure standards diluted in methanol (5 point calibration, concentrations from 0.2 to 40 ng/tube). Methanol was then flushed off with pure N2 prior to the analysis.

Relative Expanded Uncertainty: ~ ± 2.5 %
Concentration level: 2-10 ppb (m/m

ANALYSED ON DIFFERENT DAYS
Use of a calibration line.

ISSeP

For a basic estimation, we have taken into account three parameters:

- uncertainty of calibration gas mixture,
- uncertainty of repeatability and
- bias of certified mixture measurement

1 : Calibration gaSz mixture : values given by NMI
2 : Repeatability : estimated of 40 repetitions of preparation of different tubes and analysis of them on different days. In this way, we take into account uncertainty of the flowmeter, variability of tubes composition and instability of analysis system (desorption, GC and MS)
3 : Bias: estimated by comparison of the mean of the 40 measurements of different tubes and theoretical values. In this way, we take into account potential bias on the flowmeter and analysis.

REFERENCE MATERIAL:

Manufacturer: NMI

Preparation of a series of standard sampling tubes of different concentrations with this mixture, analysis of them by the same analytical method as the sample and creation of the calibration line. The flow rate was the same for all the tubes with no by-pass. We put the pure gas on the tubes.

Certification date: 8/26/2005

Expiry date: 8/26/2007

Pressure of the cylinder: 40 bars

Relative Expanded Uncertainty: ~ ± 3 %
Concentration level: ~ 100 ppb (m/m)

ANALYSED ON DIFFERENT DAYS
Use of a calibration line.

Repeatability

The working standard is a gas cylinder with compressed ambient air that is appropriate due to its comparability to a real ambient air sample. This standard was sampled 22 times consecutively to establish the repeatability of the method.

The concentrations of the VOCs in the working standard are presented as mean values of the 22 measurements together with the relative standard deviation for each compound. As presented in appendix 3 the relative standard deviation of each compound was 1-5% for most of the compounds. One exception is 1,3-butadiene, which has a relative standard deviation that exceeded 10%.
The concentrations of trans-2-pentene, n-octane and 1,2,3-trimethylbenzene were below the detection limits for these compounds and their repeatability could not be calculated. Trans-2-Pentene had a relative standard deviation of 1-6 % on the different levels in the linearity tests with the certified gas standard and 6 % is used in the uncertainty calculations. For n-octane and 1,2,3-trimethylbenzene an estimation of the relative standard deviation was made with help from the "in house" gas standards that were also used for calibration of these compounds.

Measurement Uncertainty

The overall uncertainty for each component was calculated according to the Guide to the Expression of Uncertainty in Measurement (GUM). The parameters included in the calculations were the relative standard deviation of each compound in the repeatability test, the uncertainty of the certified gas standard, the uncertainty in measurement volume and the blank uncertainty.
The uncertainty that was calculated according to GUM at relevant concentration levels is acceptable for most of the components. 1,3-butadiene and n-octane showed higher uncertainties than the other compounds. The expanded uncertainty is calculated with a coverage factor of 2 and is presented below.

compound	working standard conc. (ppb)	repeatability relative standard deviation (%)	Uncertainty calculated with a coverage factor of 2 (%)
Ethane	3.0	5	10
Ethene	7.4	3	7
Propane	82	2	5
Propene	4.0	1	5
iso-Butane	3.7	2	6
n-Butane	6.9	1	5
Ethyne	4.2	2	5
trans-2-Butene	0.54	3	7
1-Butene	0.63	3	8
iso-Butene	11	13	27
cis-2-Butene	0.60	2	6
iso-Pentane	9.6	2	5
n-Pentane	3.8	2	5
1,3-Butadiene	0.41	16	32
Propyne	0.14	30	60
t-2-Pentene	<0.12	6 *	13
c-2-Pentene	0.35	2	6
2-Metylpentane	1.3	1	5
3-Metylpentane	0.73	3	7
Isoprene	0.12	5	13
n-Hexane	0.55	3	8
Benzene	0.71	4	9
Cyclohexane	0.27	3	8
iso-Octane	3.0	1	5
n-Heptane	1.4	3	8
Toluene	9.7	2	6
n-Octane	<0.12	14 *	28
Ethylbenzene	0.49	2	6
m+p-Xylene	1.7	5	10
o-Xylene	0.56	4	9
*n-N*onane	0.10	10	20
1,3,5-Trimethylbenzene	0.24	3	8
1,2,4-Trimethylbenzene	0.59	5	11
1,2,3-Trimethylbenzene	<0.02	14*	28

REFERENCE MATERIAL

Manufacturer: NPL

The reference standard is analyzed at least 5 times with 5 different sampling volumes. The response factors are calculated RF=(area/sampling volume)/standard concentration.

Certification date: 31 January 2006

Expiry date: 31 January 2008
Pressure of the cylinder: Information not provided by the laboratory

Relative Expanded Uncertainty: ~ ± 2 %
Concentration level: 4 ppb (m/m)

ANALYSED ON DIFFERENT DAYS
Average response factor from different calibration levels.

NPL

Three sources of uncertainty are considered:

1 *Uncertainty due to analytical repeatability (Ua)*

The analysis is carried out according to an ABABA sequence. The standard deviation of the results for this sequence is calculated. When the analysis is repeated over N days, the uncertainty due to anaytical repeatability (ua) is taken as the standard error of the mean. This is expanded to allow for the limited number of degrees of freedom.

2 *Uncertainty of calibration standard (Uref)*

This is dervied from the uncertainty in the certified values of the reference standard used as the calibrant. These are shown on the sheet "CALIBRATION METHOD"

3 *Uncertainty due to linearity and chromatographic error (Ul)*

In the case of the analysis of the AMBIENT mixture, the uncertainty due to the linearity of the system (including the GC detector) is estimated. These values are included in the column headed Ul on the "RESULTS-AMBIENT AIR" sheet. There is no significant uncertainty due to linearity in the analysis of the synthetic standard, since the unknown and the standard are closely matched in concentration.

Expanded Uncertainty (U)

All of the above uncertainties are expanded (95% ci) and then combined in quadrature.

x **nmol/mol**	u_a	U_a	U_{ref}	**U**
6.72	0.5%	0.6%	1.0%	**1.2%**
6.67	0.4%	0.6%	1.0%	**1.1%**
6.66	0.6%	0.7%	1.0%	**1.2%**
6.54	0.5%	0.7%	1.0%	**1.2%**
7.07	2.3%	3.0%	1.0%	**3.1%**
6.89	0.3%	0.3%	1.0%	**1.1%**
6.78	0.6%	0.7%	1.5%	**1.7%**
6.88	0.4%	0.5%	1.0%	**1.1%**
6.79	0.9%	1.1%	1.0%	**1.5%**
6.78	0.9%	1.2%	1.0%	**1.5%**
5.13	0.8%	1.1%	1.0%	**1.5%**
5.21	0.8%	1.1%	1.0%	**1.5%**
6.64	1.0%	1.3%	1.0%	**1.6%**
4.93	0.9%	1.1%	1.0%	**1.5%**
5.03	0.6%	0.8%	1.0%	**1.3%**
5.13	0.7%	0.9%	1.0%	**1.3%**
5.16	0.6%	0.8%	1.0%	**1.3%**
5.19	0.4%	0.5%	1.5%	**1.6%**
5.06	0.8%	1.1%	1.0%	**1.5%**
4.18	0.7%	0.9%	1.0%	**1.3%**
5.19	0.2%	0.3%	1.0%	**1.0%**
5.15	0.8%	1.1%	1.0%	**1.5%**
3.61	1.3%	1.6%	1.5%	**2.2%**
3.87	1.5%	1.9%	1.5%	**2.4%**
7.62	1.2%	1.6%	1.5%	**2.2%**
3.77	1.1%	1.4%	1.5%	**2.0%**
3.69	1.1%	1.4%	2.0%	**2.4%**
3.90	2.1%	2.7%	2.0%	**3.3%**
3.53	0.5%	0.7%	2.0%	**2.1%**

Ua = ua / (SQRT/(5)) x 2.87 (d.o.f.)
U = SQRT((Ua)^2 + (Uref)^2)

REFERENCE MATERIAL:

Manufacturer: National Physical Laboratory

Direct comparison with an NPL Primary Reference Gas Mixture

Certification date: Aug-06

Expiry date: Aug-08

Pressure of the cylinder: 60 Bar

Relative Expanded Uncertainty: ~ ± 1 %
Concentration level: 4 ppb (m/m)

ANALYSED ON DIFFERENT DAYS
1 response factor.

UBA (A)

measurement uncertainty:

* uncertainty of the reference material
* uncertainty caused by varying response factors (standard deviation of the response factors)
* uncertainty caused by varying concentrations of the 5 measurements (standard deviation of the concentrations of the 5 measurements)

k = 2 is included in the given uncertainties

Calibration standard (reference material) and sample were applied under repeatable conditions; as reference material and sample showed comparable concentrations, we used one-point calibration for our measurements)

REFERENCE MATERIAL:

Manufacturer: National Physical Laboratory NPL

Direct sampling of reference material

Certification date: Aug-05

Expiry date: Aug-06

Pressure of the cylinder: 80 bar

Additional reference material 1:
Manufacturer: National Physical Laboratory NPL
Certification date: Aug. 05
Expiry date: Aug.06
APE 313679
Concentrations of the mixture of 30 hydrocarbons:
1,4 - 10,2 ppb

Additional reference material 2:
Manufacturer: Nederlands Meetinstituut NMI
Certification date: 09.02.2006
Expiry date: 09.02.2009
Number: 3220237-01
Concentrations of the mixture of 29 hydrocarbons:
9,4 - 10,8 ppb

Relative Expanded Uncertainty: ~ ± 2 %
Concentration level: 4 ppb (m/m)

CONSECUTIVE ANALYSIS
1 response factor.

VVM 1

The following are considered for the uncertainty calculations of the analytical results:

Ug concentrations of calibration gasses
Ua analyses

The combined uncertainty Utot is calculated as the square root of the sum of squares of the above mentioned uncertainties.

	Level 1 (lower concentration) %				Level 2 (higher concentration) %			
	Ug	Ua	$=Ug^2+Ua^2$	$=\sqrt{(Ug^2+Ua^2)}$	Ug	Ua	$=Ug^2+Ua^2$	$=\sqrt{(Ug^2+Ua^2)}$
ethane	2.5	88	7750	88.04	2.5	12	150	12.26
ethylene (ethene)	2.5	15	231	15.21	2.5	4	22	4.72
propane	2.5	4	22	4.72	2.5	5	31	5.59
propene	2.5	11	127	11.28	2.5	4	22	4.72
i-butane (2-methylpropane)	2.5	10	106	10.31	2.5	3	15	3.91
butane	2.5	9	87	9.34	2.5	4	22	4.72
acetylene (ethyne)	2.5	9	87	9.34	2.5	12	150	12.26
trans-2-butene	2.5	10	106	10.31	2.5	5	31	5.59
1-butene	2.5	5	31	5.59	2.5	5	31	5.59
cis-2-butene	2.5	6	42	6.50	2.5	5	31	5.59
i-pentane (2-methylbutane)	2.5	10	106	10.31	2.5	3	15	3.91
pentane	2.5	10	106	10.31	2.5	3	15	3.91
1,3-butadiene	2.5	14	202	14.22	2.5	6	42	6.50
trans-2-pentene	5	11	146	12.08	5	9	106	10.30
1-pentene	5	10	125	11.18	5	8	89	9.43
i-hexane (2-methylpentane)	5	6	61	7.81	5	8	89	9.43
hexane	2.5	15	231	15.21	2.5	8	70	8.38
isoprene (2-methyl-1,3-butadiene)	5	18	349	18.68	5	8	89	9.43
heptane	5	4	41	6.40	5	14	221	14.87
benzene	2.5	2	10	3.20	2.5	19	367	19.16
2,2,4-trimethylpentane (i-octane)	5	3	34	5.83	5	18	349	18.68
octane	5	4	41	6.40	5	18	349	18.68
toluene	2.5	2	10	3.20	2.5	19	367	19.16
ethylbenzene	2.5	4	22	4.72	2.5	12	150	12.26
m+p-xylene	5	4	41	6.40	5	11	146	12.08
o-xylene	2.5	4	22	4.72	2.5	12	150	12.26
1,3,5-trimethylbenzene	5	8	89	9.43	5	14	221	14.87
1,2,4-trimethylbenzene	5	7	74	8.60	5	14	221	14.87
1,2,3-trimethylbenzene	5	18	349	18.68	5	16	281	16.76

REFERENCE MATERIAL:

Manufacturer: Praxair

7 levels 0.537; 1.039; 1.539; 2.036; 2.530; 3.023; 3.557 ppb more analysis/ level

Certification date: 14/12/2006
Expiry date: 16/12/2009
Pressure of the cylinder: 150 bar

Relative Expanded Uncertainty: ~ ± 5 %
Concentration level:~ 200 ppb (m/m)

ANALYSED ON DIFFERENT DAYS
Use of calibration line (7 different levels of concentration).

VMM 2

For the calculation of the combined uncertainty the following uncertainties are used:

Us: sample volume
Ud: flowmeter
Uctrl: time measurement preparation control sample
Ug: concentration calibration gas
Um: mass flow controller calibration system
Ua: analysis

The combined uncertainty Utot is calculated from the square root of the sum of the squares of the mentioned uncertainties.

Level 1

	Us	Ud	Uctrl	Ug	Um	Ua	Us²	Ud²	Uctrl²	Ug²	Um²	Ua²	= som	=V‾‾‾‾‾(som)
i-butane (2-methylpropane)	5	2	0.5	4.35	1	9.74	25	4	0.25	19	1	95	144	12.00
Butane	5	2	0.5	4.35	1	9.74	25	4	0.25	19	1	95	144	12.00
acetylene (ethyne)	5	2	0.5	4.35	1	9.74	25	4	0.25	19	1	95	144	12.00
trans-2-butene	5	2	0.5	4.35	1	9.74	25	4	0.25	19	1	95	144	12.00
1-butene	5	2	0.5	4.35	1	9.74	25	4	0.25	19	1	95	144	12.00
cis-2-butene	5	2	0.5	4.35	1	9.74	25	4	0.25	19	1	95	144	12.00
i-pentane (2-methylbutane)	5	2	0.5	4.35	1	3.77	25	4	0.25	19	1	14	63	7.96
pentane	5	2	0.5	4.42	1	3.57	25	4	0.25	20	1	13	63	7.91
1,3-butadiene	5	2	0.5	4.35	1	9.74	25	4	0.25	19	1	95	144	12.00
trans-2-pentene	5	2	0.5	4.35	1	3.1	25	4	0.25	19	1	10	59	7.67
1-pentene	5	2	0.5	4.35	1	3.22	25	4	0.25	19	1	10	60	7.72
i-hexane (2-methylpentane)	5	2	0.5	4.35	1	8.89	25	4	0.25	19	1	79	128	11.32
hexane	5	2	0.5	4.42	1	6.45	25	4	0.25	20	1	42	91	9.56
isoprene	5	2	0.5	4.35	1	4.1	25	4	0.25	19	1	17	66	8.12
heptane	5	2	0.5	4.35	1	7.25	25	4	0.25	19	1	53	102	10.09
benzene	5	2	0.5	4.61	1	7.82	25	4	0.25	21	1	61	113	10.61
2,2,4-trimethylpentane (i-octane)	5	2	0.5	4.35	1	5.71	25	4	0.25	19	1	33	82	9.04
Octane	5	2	0.5	4.83	1	3.2	25	4	0.25	23	1	10	64	7.99
toluene	5	2	0.5	7.57	1	7.49	25	4	0.25	57	1	56	144	11.99
ethylbenzene	5	2	0.5	4.63	1	4.79	25	4	0.25	21	1	23	75	8.64
m+p-xylene	5	2	0.5	3.23	1	3.7	25	4	0.25	10	1	14	54	7.37
o-xylene	5	2	0.5	3.81	1	3.18	25	4	0.25	15	1	10	55	7.41
1,3,5-trimethylbenzene	5	2	0.5	4.35	1	4.33	25	4	0.25	19	1	19	68	8.24
1,2,4-trimethylbenzene	5	2	0.5	4.04	1	5.39	25	4	0.25	16	1	29	76	8.70
1,2,3-trimethylbenzene	5	2	0.5	4.04	1	5.39	25	4	0.25	16	1	29	76	8.70

Level 2

	Us	Ud	Uctrl	Ug	Um	Ua	Us²	Ud²	Uctrl²	Ug²	Um²	Ua²	= som	=V‾‾‾‾‾(som)
i-butane (2-methylpropane)	5	2	0.5	7.57	1	2.83	25	4	0.25	57	1	8	96	9.78
Butane	5	2	0.5	7.57	1	2.83	25	4	0.25	57	1	8	96	9.78
acetylene (ethyne)	5	2	0.5	7.57	1	2.83	25	4	0.25	57	1	8	96	9.78
trans-2-butene	5	2	0.5	7.57	1	2.83	25	4	0.25	57	1	8	96	9.78
1-butene	5	2	0.5	7.57	1	2.83	25	4	0.25	57	1	8	96	9.78
cis-2-butene	5	2	0.5	7.57	1	2.83	25	4	0.25	57	1	8	96	9.78
i-pentane (2-methylbutane)	5	2	0.5	4.35	1	2.65	25	4	0.25	19	1	7	56	7.50
pentane	5	2	0.5	4.42	1	3.41	25	4	0.25	20	1	12	61	7.84
1,3-butadiene	5	2	0.5	7.57	1	2.83	25	4	0.25	57	1	8	96	9.78
trans-2-pentene	5	2	0.5	4.35	1	2.27	25	4	0.25	19	1	5	54	7.37
1-pentene	5	2	0.5	4.35	1	2.51	25	4	0.25	19	1	6	55	7.45
i-hexane (2-methylpentane)	5	2	0.5	4.35	1	3.25	25	4	0.25	19	1	11	60	7.73
hexane	5	2	0.5	4.42	1	4.18	25	4	0.25	20	1	17	67	8.20
isoprene	5	2	0.5	4.35	1	2.19	25	4	0.25	19	1	5	54	7.35
heptane	5	2	0.5	4.35	1	5.48	25	4	0.25	19	1	30	79	8.90
benzene	5	2	0.5	4.61	1	3.92	25	4	0.25	21	1	15	67	8.18
2,2,4-trimethylpentane (i-octane)	5	2	0.5	4.35	1	4.61	25	4	0.25	19	1	21	70	8.39
octane	5	2	0.5	4.83	1	3.39	25	4	0.25	23	1	11	65	8.07
toluene	5	2	0.5	7.57	1	2.83	25	4	0.25	57	1	8	96	9.78
ethylbenzene	5	2	0.5	4.63	1	3.53	25	4	0.25	21	1	12	64	8.01
m+p-xylene	5	2	0.5	3.23	1	2.92	25	4	0.25	10	1	9	49	7.01
o-xylene	5	2	0.5	3.81	1	2.56	25	4	0.25	15	1	7	51	7.16
1,3,5-trimethylbenzene	5	2	0.5	4.35	1	3.41	25	4	0.25	19	1	12	61	7.80
1,2,4-trimethylbenzene	5	2	0.5	4.04	1	3.38	25	4	0.25	16	1	11	58	7.62
1,2,3-trimethylbenzene	5	2	0.5	4.04	1	3.38	25	4	0.25	16	1	11	58	7.62

REFERENCE MATERIAL:

Manufacturer: Praxair

4 level Mass Flow Controller is set on 10 cc, sample tubes are connected for 30 sec, 2 min, 4 min and 6 min
3 analysis/ level

Certification date: 7/3/2000
Expired date: 4/07/2001 (concentrations were regularly controlled by primary standards)
Pressure of the cylinder: 10 bar

Relative Expanded Uncertainty: ~ ± 5 %
Concentration level:~ 1000 ppb (m/m)

ANALYSED ON DIFFERENT DAYS
Use of different levels of concentration for calibration.

Annex IV*

Title:

Preparation and circulation of VOC gas standard mixtures for intercomparison purposes. Final Report (with supplementary information)

April 2008

Authors:

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* This Annex is an extract from an internal report of work performed by the National Physical Laboratory, Teddington, Middlesex, UK, under an EC service contract no. 382557 F1SC.

Contents

Part A(1): Preparation of synthetic VOC mixtures

The requirement was to prepare 17 mixtures in 10 litre cylinders containing the following VOCs at concentrations between 1 and 10 nmol/mol, with a dilution gas of known purity.

ethane
ethylene (ethene)
acetylene (ethyne)
propane
propene
n-butane (butane)
i-butane (isobutane or 2-methylpropane)
1-butene
trans-2-butene
cis-2-butene
1,3-butadiene
n-pentane (pentane)
i-pentane (isopentane or 2-methylbutane)
1-pentene
2-pentene
isoprene (2-methyl-1,3-butadiene)
n-hexane (hexane)
i-hexane (isohexane or 2-methylpentane)
n-heptane (heptane)
n-octane (octane)
i-octane (2,2,4-trimethylpentane)
benzene
toluene
ethylbenzene
m+p-xylene
o-xylene
1,2,4-trimethylbenzene
1,2,3-trimethylbenzene
1,3,5-trimethylbenzene

All mixtures were prepared in Air Products 10.0 litre aluminium gas cylinders, treated internally with the proprietary *Quantum passivation* process to inhibit hydrocarbon adsorption on the walls. The source of the balance gas for all mixtures is Air Products *BIP plus* nitrogen. The nitrogen is flowed through in-line filters and cold traps to remove impurities while filling.

High concentration parent cylinders (μmol/mol range) were prepared directly using source components. All components were added gravimetrically as a gas, liquefied gas or liquid, using loop injections, which involves the individual weighing of each component and the diluent nitrogen gas. The purity of the components and the purified balance gas has been assessed by gas chromatographic analysis. The concentrations of the individual hydrocarbons have been quantified from this set of weights with corrections made from the purity analysis.

Synthetic mixture cylinders and working standards were prepared gravimetrically using the high concentration parent cylinders and the high purity nitrogen balance gas. Two distinct "mother" mixtures with VOC amount fractions in the range 180 to 380 nmol/mol were used, named V3 and V4, so that there were two distinct types of synthetic mixture cylinders. The two mother mixtures are compared in Table A1 (Annex A) by comparing the response factors obtained when analysing them on the same gas chromatograph.

NPL have reviewed their uncertainty analysis for these gravimetric mixtures, a process that incorporates the results from the complete study (see Annex D). The uncertainties associated with the gravimetric preparation of these standards is significantly lower than the analytical precision to which we can measure them. The gravimetric concentrations for each cylinder are given in Table A2.

The composition of each participant cylinder was checked for stability by analysing them soon after manufacture against a working standard ("T = 0"), and again after an interval of approximately 4 months ("T = 4 months"). Each cylinder was checked for stability against a new working standard when returned to NPL to make up the 3rd round of stability. The 3rd round of analysis was approximately 12 months after the 1st round ("T = 12 months"). The new working standards were freshly diluted from the higher concentration "mother" mixtures prior to each round of analysis. The working standard concentrations were verified using a suite of NPL in-house standards.

Different gas chromatographs with slightly different methods were used in the analysis at T = 0 and T = 4 months. The method used at T = 12 months was identical to the method used at T = 4 months. The two methods are summarised in the Table below:

Apparatus	**T = 0**	**T = 4 months**
Gas Chromatograph Model	Varian 3600	Varian 3600 CX
Inlet tubing	1/16" Silcosteel tubing	1/16" Silcosteel tubing
Sample preconcentration trap	Tenax TA	Glass Beads
Trapping temperature	-99^{o}C	-165^{o}C
Column	PLOT Al_2O_3/KCl, 50m 0.53mm ID	PLOT Al_2O_3/KCl, 50m 0.53mm ID
Carrier Gas	Helium	Helium
Detector	FID	FID

These results are also presented in Table A2.

Part A(2): Cross-checking of assigned gravimetric values

The measurement of each cylinder against reference cylinders allows the gravimetric concentrations assigned to each cylinder to be checked for mislabelling or calculation errors.

The criterion for a "significant" difference for component i in cylinder j at time t = 0 is:

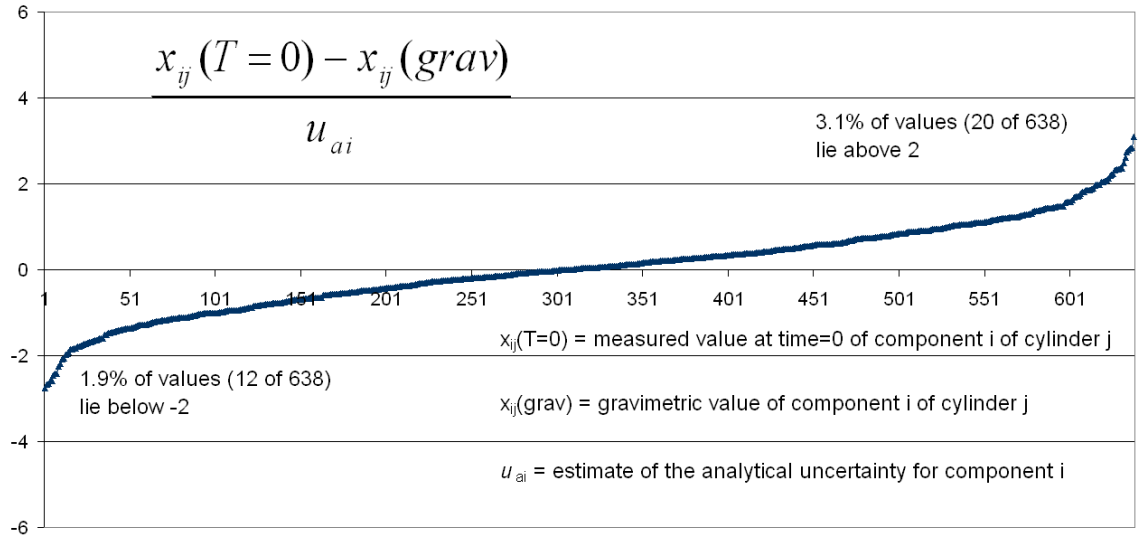
$$\left| \frac{x_{ij}(T=0) - x_{ij}(grav)}{u_{ai}} \right| > 2$$

Where 2 gives a "2 sigma" test for the modulus of the left hand side.

u_a is an estimate of the measurement uncertainty which has been evaluated over the 3 rounds of analysis using the standard deviation of the results. See Annex D for a full description of the uncertainty calculation. We would expect 5 % of the values to lie outside the range –2 < y < 2 (where y is the term inside the modulus brackets) using a confidence interval of 95% associated with this uncertainty.

The graph below shows the plot of this data for 638 data points comprised of 29 component results (of the 30 components, m-xylene and p-xylene are reported as 1 result), 2 versions and 11 cylinders in each version measured at the start of the intercomparison.

This graph shows a 2σ test for calculation of measurement difference using the square root of the average variance of the results from the 3 rounds of analysis as u_a



5% of the values lie outside of the range –2 < y < 2 so we can infer that there is no statistically significant variations in the consistencies of the gravimetric concentrations and the measured values at time t = 0.

Part A(3): Evaluation of the stability in synthetic VOC mixtures

The data from the 3 rounds of stability trials were analysed to identify any statistically significant drift. Each round of analysis was performed against a new working standard that was prepared from a high concentration parent to eliminate errors associated with drift common to the reference and test cylinders. It can be assumed that the percentage drift in these high concentration mixtures is negligible compared with percentage drifts in the low concentration mixtures.

A statistical model was drawn up that treats all cylinders as identical to calculate an estimate for the parameter of drift for each species using the 3 rounds of data at T = 0, 4 months and 12 months.

The drift test is based on the hypotheses that

- There is negligible drift in the parent mixtures (at 200 nmol/mol) from which freshly diluted reference mixtures were made at each of the three rounds.

- There is no expectation that the drift of different species will be related, therefore the statistical modelling is done for each species individually. A single drift parameter has been estimated for each version (V3 or V4) of the standard and for each species.

This last hypothesis effectively assumes that any drift is a property of the species rather than the cylinder. Any result that is an outlier from this model suggests that the cylinder may have "failed" in some way.

The drift tests are based on three sets of measurements, carried out at t = 0, 4 months and 12 months. The drift rates were estimated by fitting the model

$$\frac{x_{ij}(t=\Delta t)}{x_{iref}(t=\Delta t)} = c_{ij} + d_i^1 * \Delta t + \varepsilon_{ij}^t$$

where d_i^1 is the drift rate for species i in version 1 and c_{ij} is an offset for species i in cylinder j at time t = 0. This offset is, in effect, a check on the validity of the gravimetric values similar to that in Part A(2), but using all three measurements of each cylinder rather than just the T = 0 one. The random error in the measurement of species i in cylinder j at time t is ε_{ij}^t. The measurement of 11 cylinders of 2 versions at three times (0, 4 months and 12 months) gave 65[1] data points for each species. The model described above has 22 offsets and 2 drift rates per species (one for each version). Hence the data have 65 - 24 = 41 degrees of freedom. The model above was fitted to the data.

The residual sum of squares for the fit for each species were normalised by u_a (for that species) and compared with the expectation value of the chi-squared distribution for 41 degrees of freedom. This tests whether the ε_{ij}^t are explained by the estimated uncertainty u_a for that species. A graph showing drift estimates for all species from the two versions can be seen below:

[1] 1 cylinder was returned empty therefore reducing the number of data points from expected by 1.

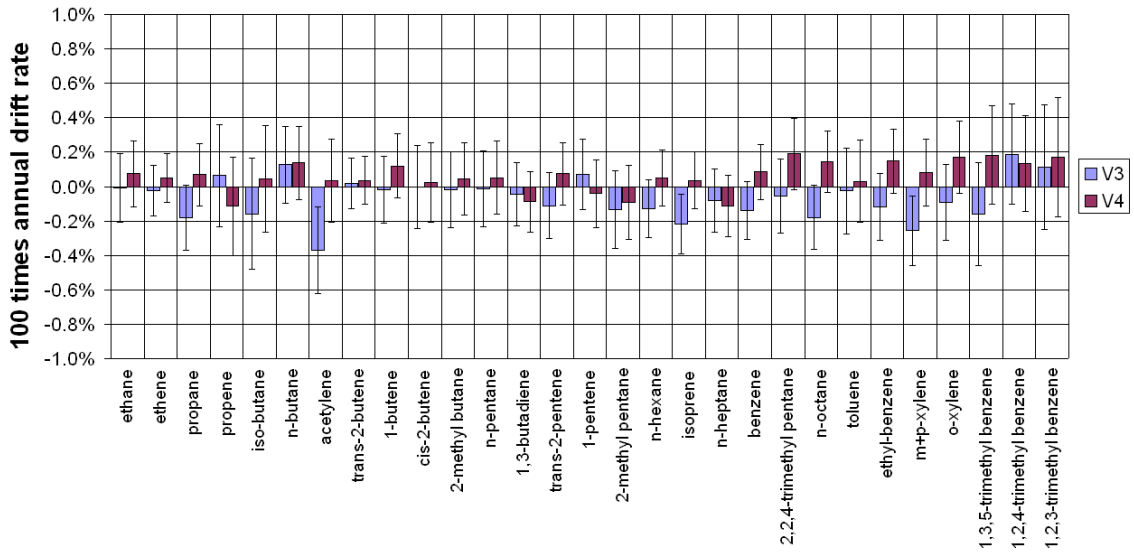


Figure 1. Estimate of the annual drift rate over 3 rounds of stability trials for two versions of 3-8ppb 30 component ozone precursor mixtures.

NOTE: In this and subsequent similar figures, a value of 1% on the y-axis means that the drift rate *d* is 0.01.

This model is an indication of any preferential drift for any given species, assuming all species have the same behaviour in all cylinders.

We have also tested for the model value for the offset (c_{ij}) with respect to its estimated uncertainty.

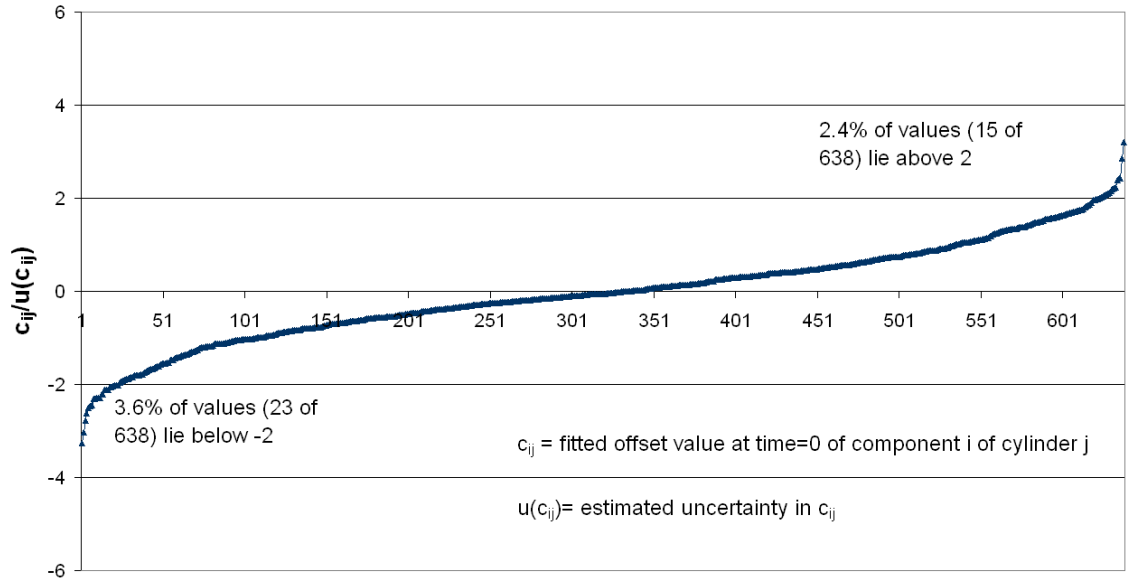


Figure 2. This chart shows the 2σ test for the fitted offset with respect to its estimated uncertainty

According to this plot there are no significant outliers exhibiting a significant offset from the gravimetric value.

Individual cylinders and individual results were examined to look for any outliers. This was done by plotting the residual deviations normalised by the analytical uncertainty, u_a as described above, as in Figure 3. No significant outliers were found.

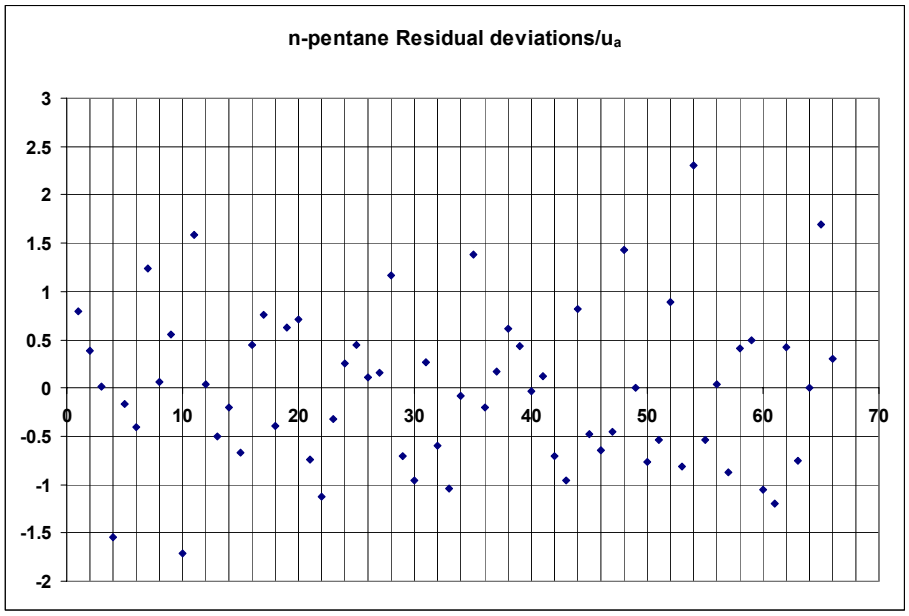


Figure 3. Plotting residual deviations normalised by the analytical measurement uncertainty provides information on outliers.

As a final test the data can be grouped per component and per cylinder to look for any major issues with stability or analytical error. The following graphs show examples of these tests.

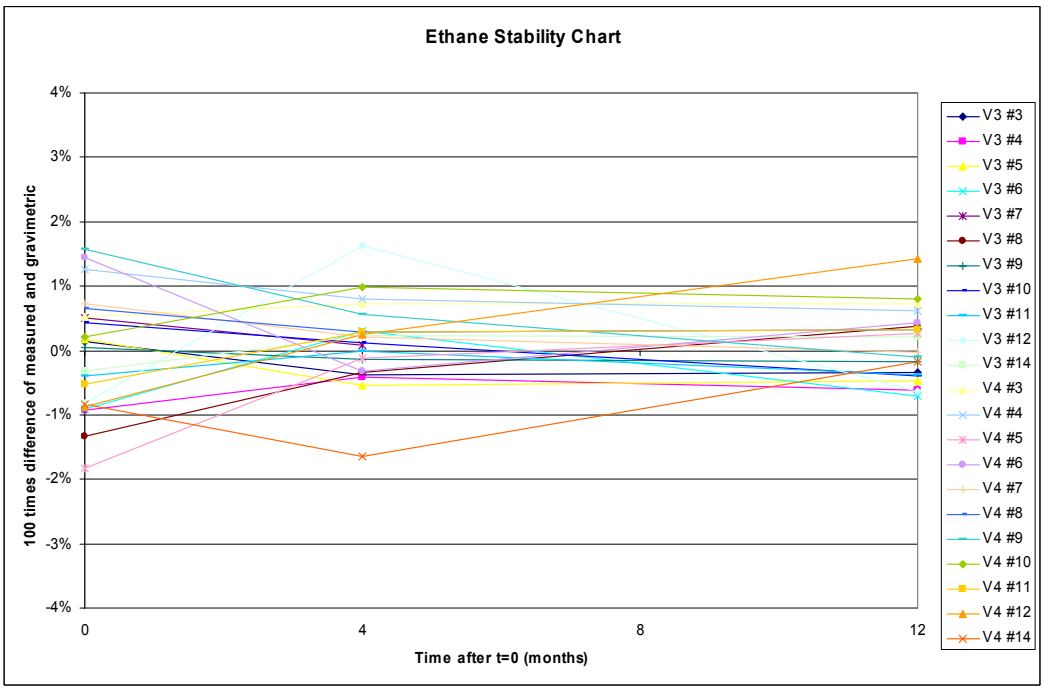


Figure 4. Small measurement uncertainty (0.51% see Annex D) leads to confident assessment of no drift in ethane in any of the cylinders.

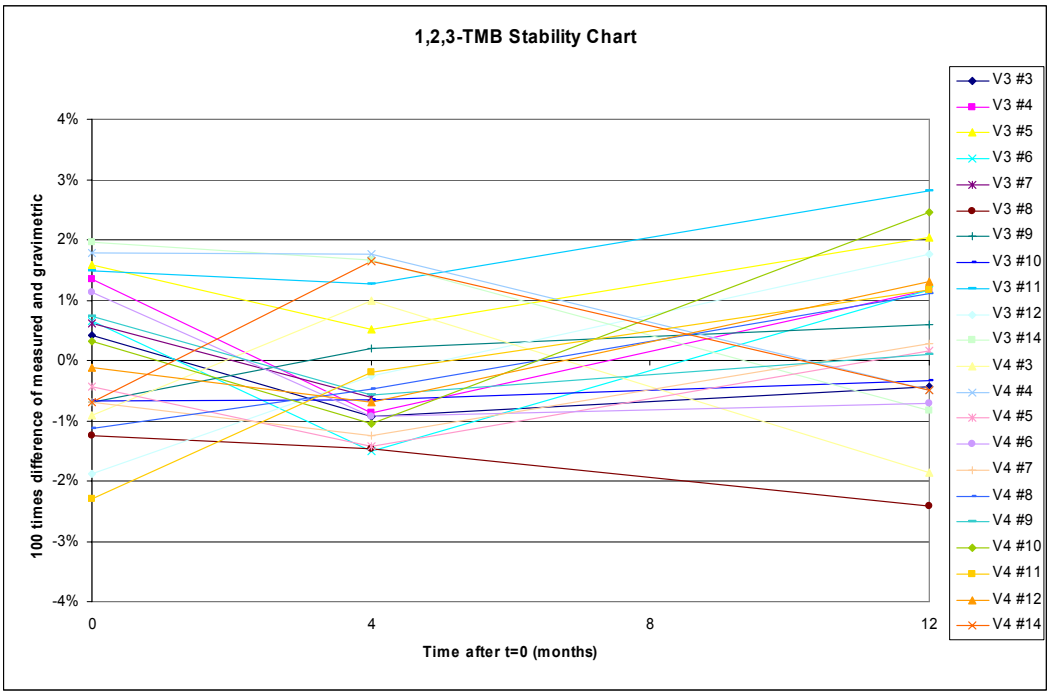


Figure 5. Here there is a greater spread of data, indicative of a more challenging component to measure (u_a 1.24% - see Annex D). There is still no obvious drift in any of the mixtures; this is backed up by the statistical drift estimate.

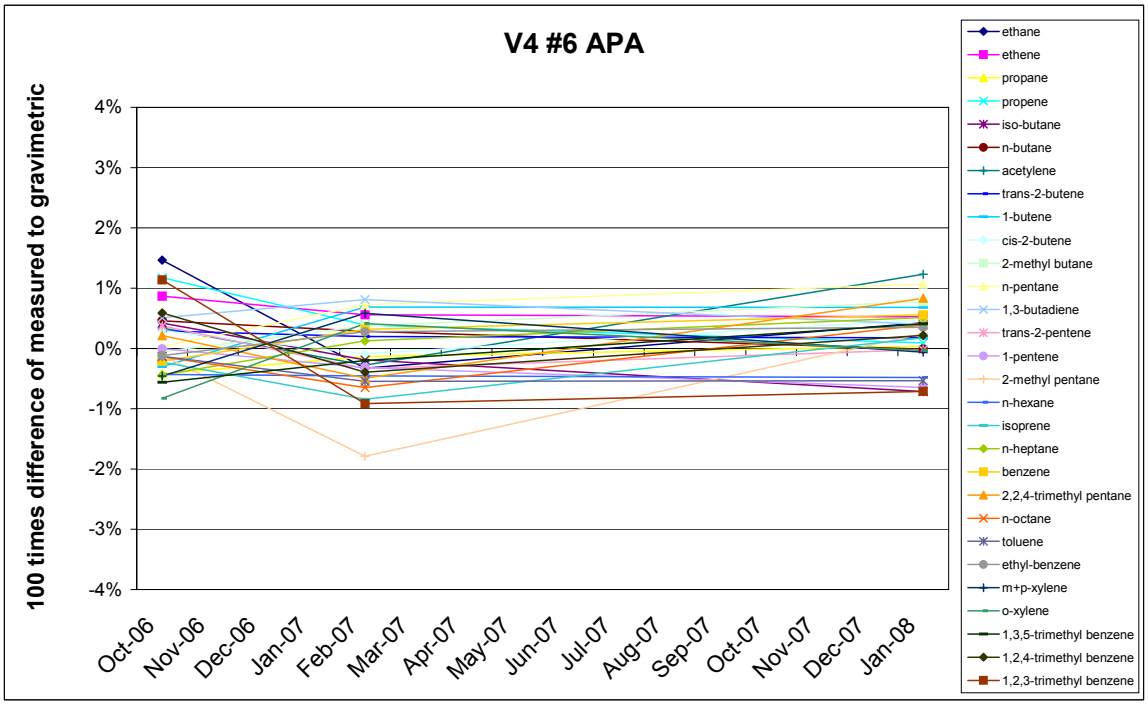


Figure 6. All data for cylinder number 6 from version 4 (Lab – Instituto do Ambiente).

A complete set of these graphs for the individual species can be found in Annex E.

Our conclusion is that there is no evidence of change in concentration in any synthetic VOC mixture that can be attributed with confidence to the stability of the mixture over the period of this study rather than to analytical measurement uncertainty.

Part B(1): Preparation of ambient VOC mixtures

All mixtures were prepared in Air Products 10.0 litre aluminium gas cylinders, treated internally with the proprietary *Quantum passivation* process to inhibit hydrocarbon adsorption on the walls.

A 50 litre Air Products cylinder with the same passivation process as previously stated was used as the mother stock for the ambient air mixtures. The mother stock was made from approximately 1% high concentration, gravimetrically prepared VOC standard and 99% whole air.

The gravimetrically added amount of high concentration VOC standard was calculated to provide between 0.1-10 nmol/mol target VOCs in the final mixture. The 50L cylinder was then filled to approximately 130 bar with whole air from Bushy Park, Teddington, using a compression pump.

A decant manifold with equivalent exit ports was assembled to transfer the mother stock into 20 x 10 litre cylinders. The rig was made from Silcosteel® tubing (Restek) and T-pieces. The decant was regulated manually to be slow and homogeneous to prevent any condensation from Joule-Thomson cooling. The final pressure in the mother stock was approximately 40 Bar and the final pressure in the 20 x 10 litre cylinders was approximately 23 Bar. The concentrations in the mother stock were determined before and after the decant, against a working gravimetric standard, and these are given in Table B1. As above, an estimate for the uncertainty has been evaluated for each component in Annex D.

Each participant's cylinder was measured by gas chromatographic analysis by comparison with a working gravimetric standard before and after the intercomparison, and the results are presented in Table B2. This stability trial was over a period of approximately 6 months. These analyses used the "T = 4 months" method for the synthetic mixtures outlined above, the only variation being that the samples were trapped at -180^{o}C instead of -165^{o}C. This was necessary to trap 100% of the ethane on the glass beads in the presence of water and other permanent gases.

Species additional to the required list, but readily identified from NPL's standards, are included in the Table in non-bold type.

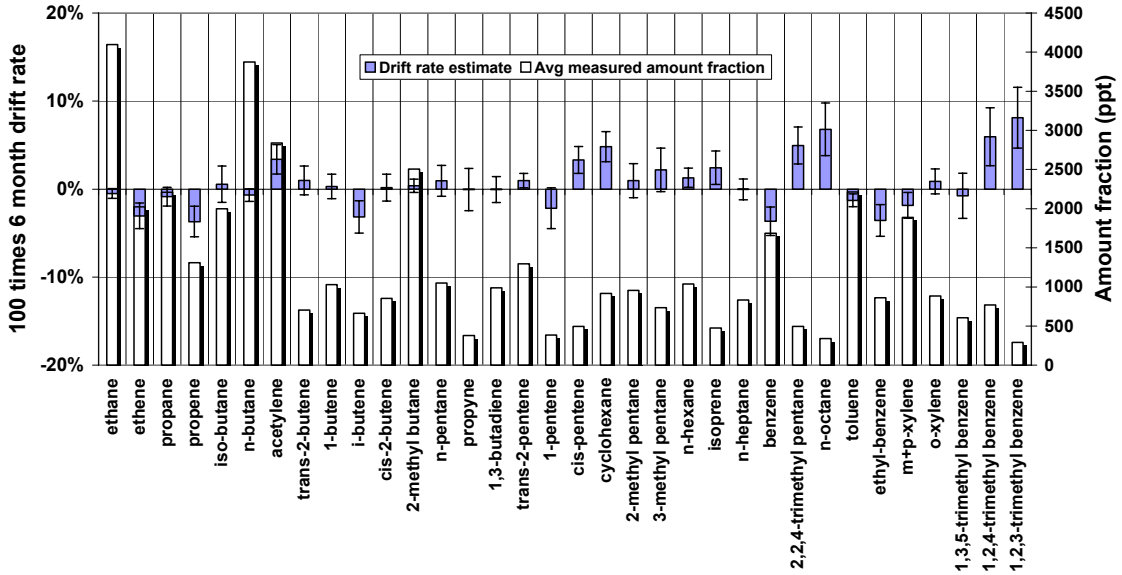
Issues of stability in these mixtures have been evaluated using statistical analysis that is outlined and discussed in this report.

The allocation of cylinders to the participants and the dates of despatch are given in Annex C.

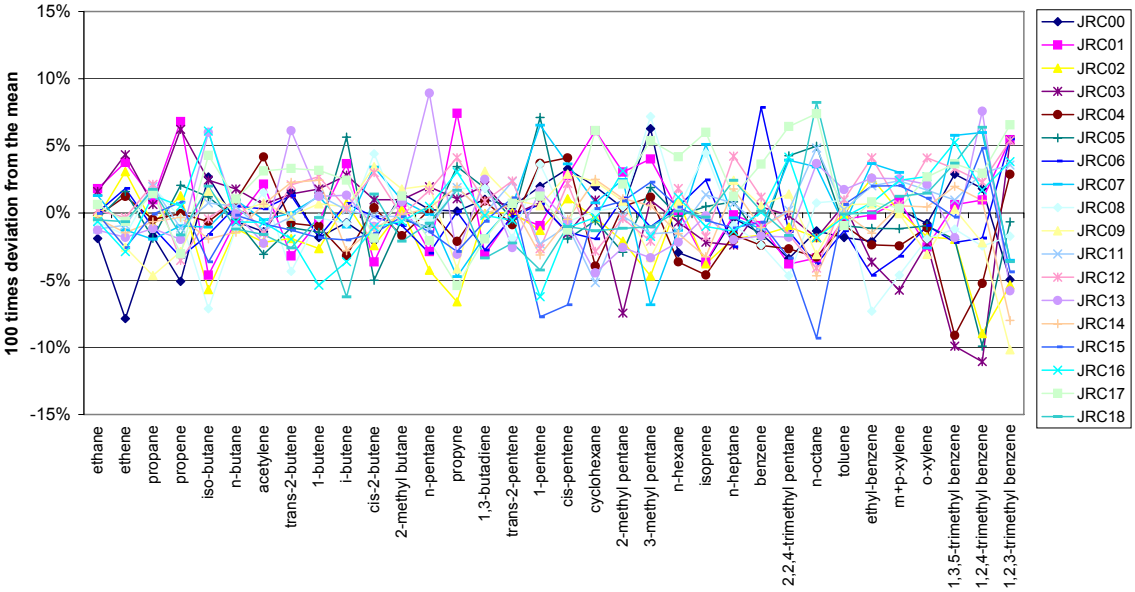
Part B(2): Evaluation of the stability in ambient VOC mixtures

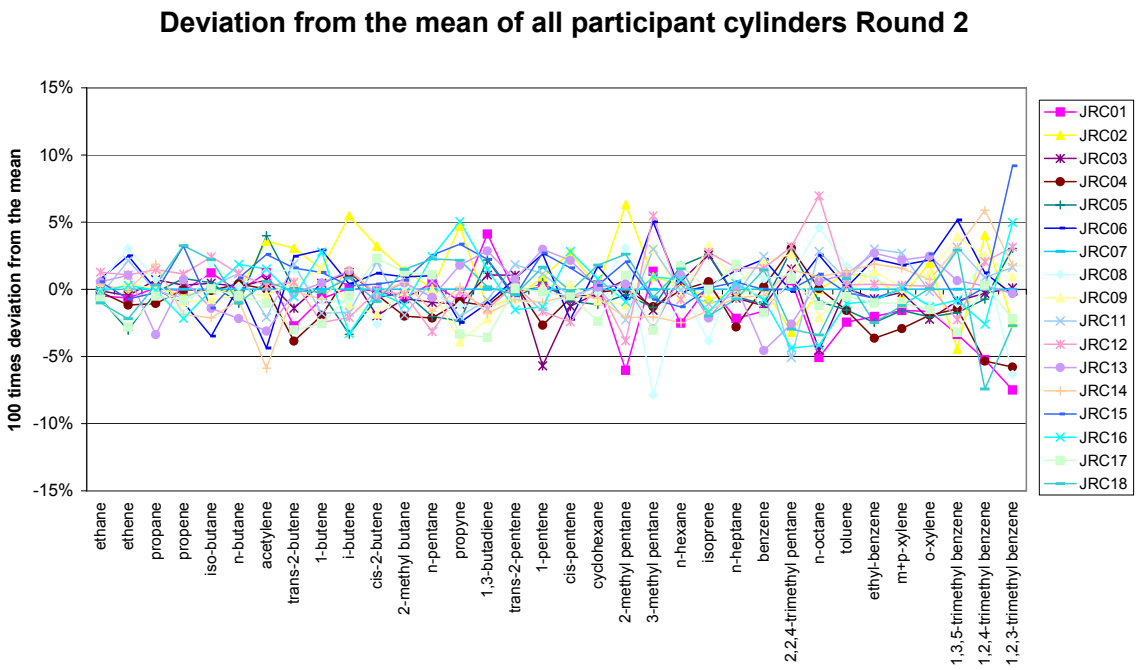
The stability of the ambient mixtures was evaluated from measurements against reference materials before and after the comparison, about 6 months apart, using a similar model to that used for the synthetic mixtures. The expanded uncertainty associated with the drift parameter in the ambient VOC standards does not include any linearity effects or bias inherent in measuring real samples. This needs to be noted when measuring challenging components, for example 1,2,3-trimethyl benzene at 0.3 ppb.

Estimate of the drift rate over 6 months and 2 rounds of stability trials for 300-4000 ppt ambient VOC standards



Deviation from the mean of all participant cylinders Round 1





The spread of data is clearly greater in the ambient mixtures compared to the synthetic mixtures. This is due to the lower concentrations and the interfering species present. The use of a desiccant was investigated, however, significant losses were observed in the compounds at the high end of the molecular weight range, and it was decided not to attempt to remove water during the analysis of these ambient samples. Water can have an effect on retention times on a PLOT Al_2O_3 column so this was noted when analysing the chromatograms.

Purging the sample preconcentration trap with carrier gas to remove permanent gases showed no obvious benefit.

A longer stability trial of the ambient mixtures would be required in order to give a clearer indication of drift in any of the species. Over the 6 month period of this study our conclusion is that there is no significant drift in any of the ambient mixtures that cannot be explained by analytical measurement uncertainties in this time frame.

Other points

One participant laboratory (AOL-UUW) returned both synthetic and ambient cylinders empty so that no final stability check could be carried out in either case.

The synthetic standard from one participant laboratory (ERLAP) had a pressure of 44 Bar when returned to NPL, significantly less than the other participants apart from AOL-UUW. Possible differential losses of VOCs, or pressure dependent effects, have not been investigated.

Annex A: Supporting data for the synthetic mixtures

Table A1: Gravimetric amount fractions (nmol/mol) of the two mother mixtures (V3 and V4), and the intercomparison percentage difference between their measured response factors.

Component	Mother V3 D95 4939	Mother V4 D95 4773	V3 versus V4
ethane	329.34	288.55	**0.75%**
ethene	327.54	286.98	**0.79%**
propane	326.06	285.70	**0.74%**
propene	323.23	283.20	**0.86%**
iso-butane	348.06	390.01	**0.64%**
n-butane	337.88	378.60	**0.58%**
acetylene	327.43	286.88	**0.35%**
trans-2-butene	337.81	378.45	**0.64%**
1-butene	332.52	372.44	**0.78%**
cis-2-butene	333.10	373.17	**0.60%**
2-methyl butane	251.08	258.95	**0.86%**
n-pentane	254.72	262.71	**0.92%**
1,3-butadiene	323.06	283.09	**0.68%**
trans-2-pentene	242.54	250.15	**0.65%**
1-pentene	247.05	254.80	**0.90%**
2-methyl pentane	251.31	259.19	**0.66%**
n-hexane	251.62	259.51	**0.49%**
isoprene	251.70	259.59	**0.50%**
n-heptane	248.42	256.22	**0.31%**
benzene	204.64	184.93	**0.73%**
2,2,4-trimethyl pentane	253.20	261.15	**0.31%**
n-octane	250.77	258.64	**0.18%**
toluene	175.96	159.02	**1.05%**
ethyl-benzene	188.03	206.30	**-0.07%**
m+p-xylene	371.95	408.09	**-0.23%**
o-xylene	184.57	202.50	**-0.09%**
1,3,5-trimethyl benzene	180.30	197.81	**-0.51%**
1,2,4-trimethyl benzene	189.07	207.44	**0.19%**
1,2,3-trimethyl benzene	172.30	189.04	**0.12%**

Table A2: Synthetic cylinder mixtures. For each cylinder, the gravimetric value and the analyses at T = 0, T = 4 months and T = 12 months are presented.

	Amount fraction (nmol/mol)							
Cylinder ref:	EV412 D95 4932				EV304 D95 4945			
Component	T = 0	T = 4 months	T = 12 months	Grav. value	T = 0	T = 4 months	T = 12 months	Grav. value
ethane	5.87	5.93	6.00	**5.92**	6.68	6.71	6.70	**6.74**
ethene	5.88	5.90	5.91	**5.88**	6.69	6.70	6.68	**6.69**
propane	5.82	5.86	5.83	**5.86**	6.60	6.64	6.66	**6.67**
propene	5.85	5.88	5.68	**5.79**	6.53	6.63	6.62	**6.60**
iso-butane	7.97	8.11	8.10	**7.97**	7.07	7.05	7.12	**7.10**
n-butane	7.67	7.76	7.77	**7.74**	6.91	6.83	6.90	**6.90**
acetylene	5.87	5.89	5.84	**5.86**	6.61	6.67	6.59	**6.68**
trans-2-butene	7.71	7.72	7.69	**7.74**	6.92	6.87	6.89	**6.89**
1-butene	7.62	7.64	7.69	**7.61**	6.76	6.75	6.76	**6.79**
cis-2-butene	7.60	7.68	7.69	**7.63**	6.85	6.83	6.82	**6.80**
2-methyl butane	5.28	5.30	5.33	**5.29**	5.11	5.12	5.16	**5.12**
n-pentane	5.33	5.33	5.44	**5.37**	5.19	5.18	5.15	**5.20**
1,3-butadiene	5.75	5.85	5.79	**5.79**	6.60	6.57	6.58	**6.59**
trans-2-pentene	5.10	5.12	5.18	**5.11**	4.94	4.97	4.93	**4.95**
1-pentene	5.23	5.20	5.25	**5.21**	5.07	5.03	5.07	**5.04**
2-methyl pentane	5.27	5.32	5.32	**5.30**	5.18	5.16	5.16	**5.13**
n-hexane	5.33	5.28	5.31	**5.30**	5.16	5.14	5.12	**5.14**
isoprene	5.32	5.31	5.33	**5.31**	5.16	5.13	5.14	**5.14**
n-heptane	5.23	5.22	5.22	**5.24**	5.10	5.05	5.02	**5.07**
benzene	3.78	3.80	3.78	**3.78**	4.15	4.17	4.14	**4.18**
2,2,4-trimethyl pentane	5.31	5.35	5.38	**5.34**	5.22	5.15	5.11	**5.17**
n-octane	5.30	5.30	5.29	**5.29**	5.15	5.09	5.13	**5.12**
toluene	3.25	3.25	3.23	**3.25**	3.56	3.59	3.60	**3.59**
ethyl-benzene	4.24	4.22	4.19	**4.22**	3.80	3.80	3.82	**3.84**
m+p-xylene	8.34	8.37	8.27	**8.34**	7.58	7.56	7.54	**7.59**
o-xylene	4.17	4.17	4.12	**4.14**	3.76	3.75	3.73	**3.77**
1,3,5-trimethyl benzene	4.05	3.99	4.12	**4.04**	3.72	3.67	3.66	**3.68**
1,2,4-trimethyl benzene	4.30	4.20	4.27	**4.24**	3.81	3.82	3.86	**3.86**
1,2,3-trimethyl benzene	3.86	3.84	3.92	**3.86**	3.56	3.49	3.56	**3.52**

	Amount fraction (nmol/mol)							
Cylinder ref:	EV305 D83 8907				EV306 D95 4965			
Component	T = 0	T = 4 months	T = 12 months	Grav. value	T = 0	T = 4 months	T = 12 months	Grav. value
ethane	6.75	6.70	6.71	**6.74**	6.68	6.76	6.69	**6.74**
ethene	6.75	6.73	6.69	**6.69**	6.73	6.71	6.71	**6.69**
propane	6.65	6.62	6.69	**6.67**	6.66	6.69	6.64	**6.67**
propene	6.54	6.57	6.59	**6.60**	6.56	6.61	6.65	**6.60**
iso-butane	7.12	7.11	7.03	**7.10**	7.01	7.24	7.14	**7.10**
n-butane	6.90	6.93	6.97	**6.89**	6.90	6.95	6.91	**6.89**
acetylene	6.77	6.63	6.70	**6.68**	6.70	6.72	6.52	**6.68**
trans-2-butene	6.88	6.89	6.90	**6.89**	6.87	6.89	6.93	**6.89**
1-butene	6.81	6.79	6.79	**6.79**	6.76	6.80	6.84	**6.79**
cis-2-butene	6.74	6.79	6.89	**6.80**	6.75	6.80	6.80	**6.80**
2-methyl butane	5.10	5.12	5.08	**5.12**	5.13	5.13	5.21	**5.12**
n-pentane	5.19	5.21	5.17	**5.20**	5.15	5.22	5.27	**5.20**
1,3-butadiene	6.58	6.59	6.52	**6.59**	6.59	6.60	6.64	**6.59**
trans-2-pentene	4.96	4.93	4.98	**4.95**	4.90	4.98	4.98	**4.95**
1-pentene	5.01	5.05	5.16	**5.04**	4.95	5.05	5.02	**5.04**
2-methyl pentane	5.12	5.14	5.11	**5.13**	5.09	5.16	5.20	**5.13**
n-hexane	5.15	5.16	5.16	**5.13**	5.05	5.12	5.16	**5.13**
isoprene	5.15	5.16	5.15	**5.14**	5.11	5.17	5.10	**5.14**
n-heptane	5.01	5.08	5.09	**5.07**	5.02	5.05	5.11	**5.07**
benzene	4.18	4.17	4.16	**4.18**	4.14	4.17	4.18	**4.18**
2,2,4-trimethyl pentane	5.19	5.15	5.18	**5.17**	5.12	5.19	5.24	**5.17**
n-octane	5.15	5.14	5.09	**5.12**	5.11	5.17	5.14	**5.12**
toluene	3.58	3.56	3.61	**3.59**	3.56	3.59	3.67	**3.59**
ethyl-benzene	3.86	3.79	3.81	**3.84**	3.85	3.79	3.84	**3.84**
m+p-xylene	7.64	7.54	7.55	**7.59**	7.66	7.59	7.60	**7.59**
o-xylene	3.81	3.73	3.76	**3.77**	3.79	3.72	3.76	**3.77**
1,3,5-trimethyl benzene	3.79	3.66	3.69	**3.68**	3.70	3.71	3.66	**3.68**
1,2,4-trimethyl benzene	3.95	3.84	3.90	**3.86**	3.83	3.85	3.95	**3.86**
1,2,3-trimethyl benzene	3.57	3.53	3.59	**3.52**	3.54	3.46	3.56	**3.52**

	Amount fraction (nmol/mol)							
Cylinder ref:	EV307 D83 8784				EV308 D95 4778			
Component	T = 0	T = 4 months	T = 12 months	Grav. value	T = 0	T = 4 months	T = 12 months	Grav. value
ethane	6.77	6.75	X	**6.74**	6.65	6.72	6.76	**6.74**
ethene	6.71	6.67	X	**6.69**	6.63	6.67	6.71	**6.69**
propane	6.80	6.65	X	**6.67**	6.70	6.63	6.62	**6.67**
propene	6.56	6.65	X	**6.60**	6.54	6.58	6.62	**6.59**
iso-butane	7.12	7.18	X	**7.10**	6.98	6.94	7.14	**7.10**
n-butane	6.89	6.96	X	**6.89**	6.84	6.93	6.86	**6.89**
acetylene	6.62	6.73	X	**6.68**	6.62	6.67	6.59	**6.68**
trans-2-butene	6.94	6.92	X	**6.89**	6.88	6.88	6.87	**6.89**
1-butene	6.81	6.78	X	**6.78**	6.83	6.78	6.76	**6.78**
cis-2-butene	6.78	6.83	X	**6.80**	6.72	6.82	6.72	**6.80**
2-methyl butane	5.10	5.10	X	**5.12**	5.04	5.13	5.06	**5.12**
n-pentane	5.19	5.20	X	**5.20**	5.18	5.24	5.17	**5.20**
1,3-butadiene	6.61	6.55	X	**6.59**	6.53	6.55	6.54	**6.59**
trans-2-pentene	4.98	4.97	X	**4.95**	4.91	4.92	4.93	**4.95**
1-pentene	5.06	5.06	X	**5.04**	5.01	5.05	5.03	**5.04**
2-methyl pentane	5.16	5.15	X	**5.13**	5.11	5.08	5.12	**5.13**
n-hexane	5.13	5.08	X	**5.13**	5.14	5.12	5.10	**5.13**
isoprene	5.15	5.09	X	**5.14**	5.14	5.15	5.12	**5.14**
n-heptane	5.13	5.02	X	**5.07**	5.06	5.06	5.00	**5.07**
benzene	4.18	4.16	X	**4.18**	4.16	4.17	4.17	**4.18**
2,2,4-trimethyl pentane	5.23	5.19	X	**5.17**	5.14	5.20	5.21	**5.17**
n-octane	5.20	5.10	X	**5.12**	5.09	5.16	5.08	**5.12**
toluene	3.61	3.56	X	**3.59**	3.60	3.54	3.58	**3.59**
ethyl-benzene	3.88	3.80	X	**3.84**	3.82	3.79	3.83	**3.84**
m+p-xylene	7.64	7.57	X	**7.59**	7.55	7.59	7.56	**7.59**
o-xylene	3.83	3.75	X	**3.77**	3.70	3.70	3.72	**3.77**
1,3,5-trimethyl benzene	3.70	3.65	X	**3.68**	3.64	3.65	3.65	**3.68**
1,2,4-trimethyl benzene	3.86	3.80	X	**3.86**	3.79	3.77	3.91	**3.86**
1,2,3-trimethyl benzene	3.54	3.49	X	**3.52**	3.47	3.46	3.43	**3.52**

	Amount fraction (nmol/mol)							
Cylinder ref:	EV309 D95 4944				EV310 D95 4968			
Component	T = 0	T = 4 months	T = 12 months	Grav. value	T = 0	T = 4 months	T = 12 months	Grav. value
ethane	6.74	6.73	6.73	**6.74**	6.77	6.75	6.71	**6.74**
ethene	6.67	6.69	6.70	**6.69**	6.77	6.63	6.68	**6.69**
propane	6.77	6.72	6.62	**6.67**	6.63	6.66	6.59	**6.67**
propene	6.58	6.44	6.54	**6.60**	6.68	6.56	6.51	**6.60**
iso-butane	7.27	7.03	7.07	**7.10**	7.04	7.06	6.96	**7.10**
n-butane	6.88	6.93	7.06	**6.89**	6.98	6.98	6.81	**6.90**
acetylene	6.73	6.58	6.70	**6.68**	6.65	6.74	6.60	**6.68**
trans-2-butene	6.89	6.91	6.89	**6.89**	6.89	6.91	6.93	**6.89**
1-butene	6.79	6.87	6.82	**6.79**	6.79	6.78	6.69	**6.79**
cis-2-butene	6.71	6.78	6.79	**6.80**	6.89	6.81	6.70	**6.80**
2-methyl butane	5.14	5.11	5.11	**5.12**	5.09	5.12	5.09	**5.12**
n-pentane	5.23	5.15	5.16	**5.20**	5.21	5.17	5.24	**5.20**
1,3-butadiene	6.62	6.61	6.64	**6.59**	6.57	6.64	6.57	**6.59**
trans-2-pentene	4.99	4.98	4.92	**4.95**	4.98	4.96	4.88	**4.95**
1-pentene	5.11	5.05	4.98	**5.04**	5.08	5.06	5.06	**5.04**
2-methyl pentane	5.18	5.17	5.17	**5.13**	5.13	5.13	5.10	**5.13**
n-hexane	5.12	5.15	5.10	**5.13**	5.18	5.12	5.13	**5.13**
isoprene	5.18	5.12	5.07	**5.14**	5.16	5.14	5.10	**5.14**
n-heptane	5.09	5.11	5.09	**5.07**	5.06	5.06	5.07	**5.07**
benzene	4.16	4.14	4.21	**4.18**	4.20	4.20	4.13	**4.18**
2,2,4-trimethyl pentane	5.18	5.20	5.25	**5.17**	5.21	5.15	5.16	**5.17**
n-octane	5.10	5.15	5.07	**5.12**	5.16	5.14	5.03	**5.12**
toluene	3.65	3.59	3.59	**3.59**	3.61	3.62	3.55	**3.59**
ethyl-benzene	3.79	3.82	3.80	**3.84**	3.84	3.85	3.82	**3.84**
m+p-xylene	7.63	7.59	7.55	**7.59**	7.58	7.71	7.61	**7.59**
o-xylene	3.78	3.75	3.72	**3.77**	3.73	3.80	3.75	**3.77**
1,3,5-trimethyl benzene	3.76	3.66	3.73	**3.68**	3.67	3.71	3.70	**3.68**
1,2,4-trimethyl benzene	3.91	3.86	3.86	**3.86**	3.80	3.89	3.86	**3.86**
1,2,3-trimethyl benzene	3.49	3.52	3.54	**3.52**	3.49	3.49	3.50	**3.52**

	Amount fraction (nmol/mol)							
Cylinder ref:	EV311 D95 4937				EV312 D95 4804			
Component	T = 0	T = 4 months	T = 12 months	Grav. value	T = 0	T = 4 months	T = 12 months	Grav. value
ethane	6.72	6.74	6.72	**6.74**	6.69	6.85	6.70	**6.74**
ethene	6.78	6.69	6.70	**6.70**	6.68	6.68	6.71	**6.69**
propane	6.73	6.71	6.70	**6.67**	6.63	6.65	6.59	**6.67**
propene	6.51	6.64	6.66	**6.60**	6.62	6.62	6.56	**6.60**
iso-butane	6.98	7.04	7.01	**7.10**	7.10	7.12	6.94	**7.10**
n-butane	6.73	6.91	6.95	**6.90**	6.92	6.89	6.93	**6.89**
acetylene	6.70	6.65	6.62	**6.68**	6.62	6.67	6.63	**6.68**
trans-2-butene	6.83	6.86	6.87	**6.90**	6.91	6.88	6.88	**6.89**
1-butene	6.80	6.68	6.76	**6.79**	6.78	6.76	6.82	**6.79**
cis-2-butene	6.70	6.83	6.76	**6.80**	6.75	6.77	6.80	**6.80**
2-methyl butane	5.14	5.16	5.12	**5.12**	5.08	5.02	5.15	**5.12**
n-pentane	5.24	5.23	5.19	**5.20**	5.12	5.16	5.27	**5.20**
1,3-butadiene	6.60	6.58	6.57	**6.59**	6.58	6.60	6.67	**6.59**
trans-2-pentene	4.97	4.93	4.95	**4.95**	4.89	4.88	4.93	**4.95**
1-pentene	5.02	5.07	5.03	**5.04**	5.00	5.04	5.02	**5.04**
2-methyl pentane	5.14	5.16	5.08	**5.13**	5.07	5.09	5.04	**5.13**
n-hexane	5.14	5.14	5.11	**5.14**	5.10	5.11	5.05	**5.13**
isoprene	5.17	5.13	5.13	**5.14**	5.11	5.09	5.12	**5.14**
n-heptane	5.08	5.03	5.02	**5.07**	5.06	5.04	5.08	**5.07**
benzene	4.18	4.18	4.15	**4.18**	4.16	4.19	4.18	**4.18**
2,2,4-trimethyl pentane	5.20	5.20	5.10	**5.17**	5.13	5.16	5.16	**5.17**
n-octane	5.14	5.14	5.16	**5.12**	5.15	5.10	5.10	**5.12**
toluene	3.62	3.59	3.61	**3.59**	3.58	3.56	3.59	**3.59**
ethyl-benzene	3.87	3.85	3.83	**3.84**	3.82	3.82	3.83	**3.84**
m+p-xylene	7.66	7.64	7.59	**7.59**	7.59	7.57	7.48	**7.59**
o-xylene	3.83	3.75	3.80	**3.77**	3.78	3.75	3.78	**3.77**
1,3,5-trimethyl benzene	3.77	3.68	3.69	**3.68**	3.63	3.63	3.74	**3.68**
1,2,4-trimethyl benzene	3.90	3.90	3.92	**3.86**	3.83	3.84	3.84	**3.86**
1,2,3-trimethyl benzene	3.57	3.56	3.62	**3.52**	3.45	3.51	3.58	**3.52**

	Amount fraction (nmol/mol)							
Cylinder ref:	EV403 D95 4790				EV411 D95 4934			
Component	T = 0	T = 4 months	T = 12 months	Grav. value	T = 0	T = 4 months	T = 12 months	Grav. value
ethane	5.95	5.96	5.96	**5.92**	5.89	5.93	5.94	**5.92**
ethene	5.89	5.91	5.89	**5.88**	5.84	5.83	5.87	**5.88**
propane	5.89	5.85	5.90	**5.86**	5.80	5.83	5.91	**5.86**
propene	5.76	5.79	5.74	**5.79**	5.80	5.72	5.73	**5.79**
iso-butane	8.05	7.90	8.01	**7.97**	7.90	7.97	8.15	**7.97**
n-butane	7.79	7.69	7.78	**7.74**	7.81	7.73	7.75	**7.74**
acetylene	5.82	5.79	5.81	**5.86**	5.90	5.90	5.84	**5.86**
trans-2-butene	7.74	7.68	7.89	**7.73**	7.76	7.71	7.70	**7.73**
1-butene	7.66	7.65	7.64	**7.61**	7.60	7.61	7.50	**7.61**
cis-2-butene	7.65	7.68	7.61	**7.63**	7.62	7.64	7.61	**7.63**
2-methyl butane	5.31	5.30	5.29	**5.29**	5.28	5.25	5.27	**5.29**
n-pentane	5.39	5.39	5.40	**5.37**	5.36	5.30	5.34	**5.37**
1,3-butadiene	5.79	5.78	5.68	**5.79**	5.86	5.76	5.81	**5.79**
trans-2-pentene	5.11	5.14	5.14	**5.11**	5.10	5.09	5.08	**5.11**
1-pentene	5.20	5.24	5.14	**5.21**	5.19	5.17	5.15	**5.21**
2-methyl pentane	5.29	5.26	5.24	**5.30**	5.33	5.22	5.20	**5.30**
n-hexane	5.31	5.28	5.29	**5.30**	5.36	5.28	5.30	**5.30**
isoprene	5.25	5.31	5.24	**5.31**	5.39	5.25	5.32	**5.31**
n-heptane	5.21	5.22	5.20	**5.24**	5.30	5.21	5.17	**5.24**
benzene	3.76	3.80	3.81	**3.78**	3.80	3.76	3.78	**3.78**
2,2,4-trimethyl pentane	5.27	5.36	5.36	**5.34**	5.39	5.32	5.32	**5.34**
n-octane	5.24	5.25	5.29	**5.29**	5.32	5.26	5.28	**5.29**
toluene	3.23	3.25	3.22	**3.25**	3.25	3.20	3.19	**3.25**
ethyl-benzene	4.20	4.22	4.22	**4.22**	4.20	4.20	4.23	**4.22**
m+p-xylene	8.31	8.40	8.36	**8.34**	8.37	8.30	8.30	**8.34**
o-xylene	4.09	4.13	4.14	**4.14**	4.18	4.10	4.14	**4.14**
1,3,5-trimethyl benzene	4.04	4.07	4.01	**4.04**	3.96	4.03	4.07	**4.04**
1,2,4-trimethyl benzene	4.24	4.27	4.23	**4.24**	4.30	4.20	4.29	**4.24**
1,2,3-trimethyl benzene	3.83	3.90	3.79	**3.86**	3.78	3.86	3.91	**3.86**

	Amount fraction (nmol/mol)							
Cylinder ref:	EV410 D95 4947				EV406 D83 8930			
Component	T = 0	T = 4 months	T = 12 months	Grav. value	T = 0	T = 4 months	T = 12 months	Grav. value
ethane	5.93	5.98	5.96	**5.92**	6.01	5.90	5.94	**5.92**
ethene	5.86	5.89	5.88	**5.88**	5.93	5.91	5.91	**5.88**
propane	5.81	5.86	5.90	**5.86**	5.84	5.85	5.86	**5.86**
propene	5.79	5.70	5.85	**5.79**	5.86	5.81	5.80	**5.79**
iso-butane	7.99	7.96	7.96	**7.97**	8.01	7.96	7.92	**7.97**
n-butane	7.76	7.75	7.83	**7.74**	7.78	7.76	7.74	**7.74**
acetylene	5.86	5.85	5.88	**5.86**	5.89	5.85	5.94	**5.87**
trans-2-butene	7.77	7.73	7.71	**7.74**	7.76	7.75	7.75	**7.74**
1-butene	7.63	7.59	7.60	**7.61**	7.59	7.67	7.67	**7.62**
cis-2-butene	7.66	7.76	7.70	**7.63**	7.65	7.62	7.67	**7.63**
2-methyl butane	5.33	5.33	5.27	**5.29**	5.29	5.31	5.34	**5.29**
n-pentane	5.39	5.37	5.34	**5.37**	5.37	5.41	5.43	**5.37**
1,3-butadiene	5.84	5.83	5.86	**5.79**	5.82	5.84	5.81	**5.79**
trans-2-pentene	5.13	5.13	5.12	**5.11**	5.13	5.10	5.11	**5.11**
1-pentene	5.21	5.25	5.25	**5.21**	5.21	5.19	5.18	**5.21**
2-methyl pentane	5.30	5.33	5.33	**5.30**	5.29	5.20	5.31	**5.30**
n-hexane	5.32	5.30	5.29	**5.30**	5.28	5.28	5.28	**5.31**
isoprene	5.35	5.29	5.32	**5.31**	5.30	5.26	5.32	**5.31**
n-heptane	5.27	5.22	5.29	**5.24**	5.22	5.25	5.27	**5.24**
benzene	3.78	3.77	3.77	**3.78**	3.77	3.79	3.80	**3.78**
2,2,4-trimethyl pentane	5.35	5.36	5.32	**5.34**	5.35	5.31	5.38	**5.34**
n-octane	5.32	5.29	5.39	**5.29**	5.28	5.25	5.31	**5.29**
toluene	3.27	3.25	3.30	**3.25**	3.25	3.23	3.23	**3.25**
ethyl-benzene	4.25	4.19	4.24	**4.22**	4.21	4.23	4.23	**4.22**
m+p-xylene	8.36	8.32	8.40	**8.34**	8.31	8.39	8.34	**8.34**
o-xylene	4.16	4.12	4.20	**4.14**	4.11	4.16	4.14	**4.14**
1,3,5-trimethyl benzene	4.10	4.02	4.05	**4.04**	4.02	4.04	4.06	**4.04**
1,2,4-trimethyl benzene	4.28	4.21	4.27	**4.24**	4.27	4.22	4.25	**4.24**
1,2,3-trimethyl benzene	3.88	3.82	3.96	**3.86**	3.91	3.83	3.84	**3.87**

	Amount fraction (nmol/mol)							
Cylinder ref:	EV407 D95 4775				EV408 D95 4936			
Component	T = 0	T = 4 months	T = 12 months	Grav. value	T = 0	T = 4 months	T = 12 months	Grav. value
ethane	5.96	5.93	5.92	**5.92**	5.96	5.93	5.94	**5.92**
ethene	5.86	5.89	5.91	**5.88**	5.91	5.89	5.88	**5.88**
propane	5.86	5.89	5.85	**5.86**	5.89	5.88	5.85	**5.86**
propene	5.77	5.80	5.70	**5.79**	5.77	5.84	5.74	**5.79**
iso-butane	7.94	7.91	7.90	**7.97**	7.98	7.95	7.84	**7.97**
n-butane	7.71	7.76	7.73	**7.74**	7.76	7.77	7.80	**7.74**
acetylene	5.81	5.95	5.82	**5.86**	5.89	5.92	5.77	**5.86**
trans-2-butene	7.64	7.74	7.69	**7.74**	7.74	7.72	7.72	**7.74**
1-butene	7.62	7.62	7.56	**7.61**	7.62	7.57	7.61	**7.61**
cis-2-butene	7.54	7.66	7.56	**7.63**	7.64	7.60	7.53	**7.63**
2-methyl butane	5.24	5.31	5.23	**5.29**	5.30	5.32	5.30	**5.29**
n-pentane	5.37	5.38	5.31	**5.37**	5.40	5.39	5.33	**5.37**
1,3-butadiene	5.74	5.80	5.75	**5.79**	5.79	5.85	5.79	**5.79**
trans-2-pentene	5.08	5.15	5.07	**5.11**	5.11	5.15	5.10	**5.11**
1-pentene	5.18	5.18	5.15	**5.21**	5.21	5.21	5.22	**5.21**
2-methyl pentane	5.28	5.33	5.24	**5.30**	5.30	5.27	5.21	**5.30**
n-hexane	5.30	5.28	5.33	**5.30**	5.32	5.32	5.30	**5.30**
isoprene	5.32	5.32	5.28	**5.31**	5.31	5.28	5.34	**5.31**
n-heptane	5.21	5.23	5.15	**5.24**	5.22	5.25	5.20	**5.24**
benzene	3.76	3.73	3.74	**3.78**	3.74	3.77	3.77	**3.78**
2,2,4-trimethyl pentane	5.29	5.34	5.30	**5.34**	5.37	5.35	5.30	**5.34**
n-octane	5.26	5.31	5.26	**5.29**	5.28	5.30	5.30	**5.29**
toluene	3.22	3.21	3.23	**3.25**	3.25	3.25	3.31	**3.25**
ethyl-benzene	4.17	4.15	4.22	**4.22**	4.21	4.21	4.30	**4.22**
m+p-xylene	8.26	8.22	8.34	**8.34**	8.35	8.29	8.44	**8.34**
o-xylene	4.11	4.12	4.11	**4.14**	4.12	4.13	4.17	**4.14**
1,3,5-trimethyl benzene	4.05	3.98	4.01	**4.04**	4.07	3.99	4.07	**4.04**
1,2,4-trimethyl benzene	4.21	4.15	4.23	**4.24**	4.26	4.20	4.31	**4.24**
1,2,3-trimethyl benzene	3.84	3.82	3.87	**3.86**	3.82	3.85	3.91	**3.86**

	Amount fraction (nmol/mol)							
Cylinder ref:	EV409 D83 8781				EV414 D29 2405			
Component	T = 0	T = 4 months	T = 12 months	Grav. value	T = 0	T = 4 months	T = 12 months	Grav. value
ethane	6.01	5.95	5.91	**5.92**	5.87	5.82	5.91	**5.92**
ethene	5.92	5.87	5.87	**5.88**	5.85	5.84	5.92	**5.87**
propane	5.97	5.89	5.87	**5.86**	5.90	5.82	5.83	**5.86**
propene	5.83	5.80	5.74	**5.79**	5.64	5.73	5.81	**5.79**
iso-butane	8.06	7.94	8.02	**7.97**	8.00	8.10	7.90	**7.97**
n-butane	7.74	7.81	7.82	**7.74**	7.62	7.74	7.85	**7.74**
acetylene	5.86	5.80	5.88	**5.86**	5.83	5.88	5.97	**5.86**
trans-2-butene	7.74	7.72	7.80	**7.74**	7.78	7.73	7.75	**7.73**
1-butene	7.64	7.55	7.75	**7.61**	7.58	7.66	7.68	**7.61**
cis-2-butene	7.70	7.64	7.80	**7.63**	7.61	7.53	7.70	**7.63**
2-methyl butane	5.29	5.27	5.33	**5.29**	5.28	5.25	5.32	**5.29**
n-pentane	5.36	5.38	5.40	**5.37**	5.28	5.36	5.34	**5.37**
1,3-butadiene	5.82	5.78	5.82	**5.79**	5.80	5.76	5.77	**5.79**
trans-2-pentene	5.11	5.15	5.14	**5.11**	5.11	5.08	5.14	**5.11**
1-pentene	5.22	5.22	5.18	**5.21**	5.19	5.21	5.20	**5.21**
2-methyl pentane	5.30	5.31	5.25	**5.30**	5.23	5.29	5.32	**5.30**
n-hexane	5.30	5.34	5.37	**5.30**	5.27	5.31	5.32	**5.30**
isoprene	5.33	5.31	5.37	**5.31**	5.30	5.33	5.33	**5.30**
n-heptane	5.26	5.24	5.26	**5.24**	5.24	5.24	5.26	**5.24**
benzene	3.81	3.73	3.83	**3.78**	3.78	3.78	3.79	**3.78**
2,2,4-trimethyl pentane	5.34	5.31	5.43	**5.34**	5.30	5.32	5.42	**5.34**
n-octane	5.31	5.26	5.35	**5.29**	5.24	5.29	5.32	**5.29**
toluene	3.29	3.24	3.29	**3.25**	3.22	3.25	3.26	**3.25**
ethyl-benzene	4.30	4.22	4.24	**4.22**	4.22	4.25	4.26	**4.22**
m+p-xylene	8.46	8.27	8.42	**8.34**	8.34	8.44	8.44	**8.34**
o-xylene	4.15	4.10	4.18	**4.14**	4.14	4.11	4.18	**4.14**
1,3,5-trimethyl benzene	4.10	4.01	4.08	**4.04**	4.01	4.05	4.09	**4.04**
1,2,4-trimethyl benzene	4.35	4.20	4.30	**4.24**	4.24	4.23	4.26	**4.24**
1,2,3-trimethyl benzene	3.89	3.84	3.87	**3.86**	3.84	3.93	3.84	**3.86**

Annex B: Supporting data for the ambient mixtures

Table B1: Ambient air mixture mother stock analytical concentrations before and after decant, and the averaged concentrations in the 17 daughter cylinders at t = 0 and t ≈ 6 months. The average consists of 16 cylinders at t ≈ 6 months as one participant cylinder was returned empty.

	Mother Stock D25 5975 amount fraction (nmol/mol)		Mean amount fraction of 17 daughter cylinders (nmol/mol)	
Component	Before Decant	After Decant	T = 0	T = 6 months
ethane	4.00	4.18	4.10	4.08
ethene	2.30	2.18	2.02	1.96
propane	2.38	2.25	2.20	2.19
propene	1.67	1.38	1.31	1.26
iso-butane	2.12	1.94	1.99	2.01
n-butane	3.93	3.90	3.88	3.85
acetylene	3.15	2.88	2.84	2.94
trans-2-butene	0.74	0.69	0.70	0.71
1-butene	1.15	1.05	1.03	1.03
i-butene	0.85	0.67	0.66	0.64
cis-2-butene	0.87	0.87	0.86	0.86
2-methyl butane	2.49	2.47	2.51	2.52
n-pentane	1.08	1.05	1.05	1.06
propyne	0.39	0.38	0.38	0.38
1,3-butadiene	1.01	0.98	0.98	0.99
trans-2-pentene	1.29	1.29	1.29	1.31
1-pentene	0.41	0.38	0.39	0.38
cis-pentene	0.50	0.48	0.50	0.51
cyclohexane	0.95	0.90	0.92	0.96
2-methyl pentane	0.94	0.95	0.96	0.96
3-methyl pentane	0.68	0.69	0.73	0.75
n-hexane	1.04	1.07	1.04	1.05
isoprene	0.48	0.49	0.48	0.49
n-heptane	0.83	0.84	0.83	0.83
benzene	1.72	1.71	1.69	1.63
2,2,4-trimethyl pentane	0.48	0.51	0.50	0.52
n-octane	0.34	0.35	0.34	0.36
toluene	2.28	2.25	2.21	2.19
ethyl-benzene	1.04	0.88	0.86	0.83
m+p-xylene	1.84	1.88	1.88	1.85
o-xylene	0.84	0.89	0.88	0.89
1,3,5-trimethyl benzene	0.57	0.59	0.61	0.60
1,2,4-trimethyl benzene	0.73	0.76	0.77	0.82
1,2,3-trimethyl benzene	0.26	0.31	0.29	0.32

Table B2: Ambient air mixture cylinders measured initial concentrations and measured concentrations after return to NPL. The values not in bold type are species additional to the species in the synthetic mixtures.

Cylinder ref:	D6 1748		D6 1849		D6 1773	
DATE	**11-May-07**	**7-Feb-08**	**15-May-07**	**8-Nov-07**	**16-May-07**	**15-Nov-07**
Component	Amount fraction (nmol/mol)					
ethane	**4.18**	**4.06**	**4.09**	**4.08**	**4.17**	**4.07**
ethene	**2.10**	**1.95**	**2.08**	**1.96**	**2.11**	**1.95**
propane	**2.23**	**2.19**	**2.19**	**2.19**	**2.22**	**2.21**
propene	**1.40**	**1.26**	**1.33**	**1.26**	**1.40**	**1.27**
iso-butane	**1.91**	**2.04**	**1.89**	**2.01**	**2.05**	**2.02**
n-butane	**3.85**	**3.84**	**3.83**	**3.84**	**3.95**	**3.85**
acetylene	**2.90**	**2.97**	**2.78**	**3.05**	**2.86**	**2.96**
trans-2-butene	**0.68**	**0.69**	**0.69**	**0.73**	**0.71**	**0.70**
1-butene	**1.02**	**1.03**	**1.00**	**1.05**	**1.05**	**1.04**
i-butene	0.69	0.64	0.67	0.68	0.68	0.65
cis-2-butene	**0.83**	**0.85**	**0.84**	**0.88**	**0.86**	**0.84**
2-methyl butane	**2.53**	**2.50**	**2.51**	**2.55**	**2.53**	**2.50**
n-pentane	**1.02**	**1.07**	**1.01**	**1.06**	**1.07**	**1.05**
propyne	0.41	0.38	0.35	0.40	0.38	0.38
1,3-butadiene	**0.96**	**1.03**	**0.99**	**0.97**	**1.01**	**1.00**
trans-2-pentene	**1.29**	**1.30**	**1.30**	**1.30**	**1.29**	**1.32**
1-pentene	**0.38**	**0.38**	**0.38**	**0.38**	**0.39**	**0.36**
cis-pentene	0.51	0.51	0.50	0.53	0.49	0.51
cyclohexane	0.98	0.97	0.91	0.96	0.93	0.96
2-methyl pentane	**0.99**	**0.91**	**0.94**	**1.03**	**0.89**	**0.97**
3-methyl pentane	0.76	0.76	0.70	0.76	0.74	0.74
n-hexane	**1.04**	**1.03**	**1.05**	**1.06**	**1.03**	**1.06**
isoprene	**0.46**	**0.49**	**0.46**	**0.48**	**0.47**	**0.50**
n-heptane	**0.83**	**0.81**	**0.82**	**0.83**	**0.81**	**0.83**
benzene	**1.67**	**1.60**	**1.66**	**1.63**	**1.69**	**1.61**
2,2,4-trimethyl pentane	**0.48**	**0.52**	**0.49**	**0.50**	**0.49**	**0.53**
n-octane	**0.33**	**0.35**	**0.34**	**0.36**	**0.34**	**0.35**
toluene	**2.20**	**2.13**	**2.21**	**2.21**	**2.23**	**2.19**
ethyl-benzene	**0.86**	**0.81**	**0.89**	**0.84**	**0.83**	**0.82**
m+p-xylene	**1.91**	**1.82**	**1.89**	**1.84**	**1.79**	**1.85**
o-xylene	**0.86**	**0.88**	**0.87**	**0.91**	**0.86**	**0.87**
1,3,5-trimethyl benzene	**0.61**	**0.58**	**0.60**	**0.58**	**0.55**	**0.60**
1,2,4-trimethyl benzene	**0.78**	**0.78**	**0.71**	**0.85**	**0.70**	**0.81**
1,2,3-trimethyl benzene	**0.31**	**0.29**	**0.28**	**0.31**	**0.31**	**0.32**

Cylinder ref:	D6 1815		D6 1804		D95 4770	
DATE	**17-May-07**	**4-Mar-08**	**18-May-07**	**16-Nov-07**	**21-May-07**	**29-Oct-07**
Component	Amount fraction (nmol/mol)					
ethane	**4.09**	**4.07**	**4.08**	**4.05**	**4.10**	**4.11**
ethene	**2.05**	**1.94**	**2.05**	**1.90**	**2.06**	**2.01**
propane	**2.20**	**2.17**	**2.17**	**2.19**	**2.18**	**2.19**
propene	**1.31**	**1.26**	**1.34**	**1.27**	**1.27**	**1.25**
iso-butane	**1.98**	**2.01**	**2.02**	**2.02**	**1.97**	**1.94**
n-butane	**3.91**	**3.86**	**3.86**	**3.81**	**3.90**	**3.86**
acetylene	**2.96**	**2.94**	**2.75**	**3.06**	**2.85**	**2.81**
trans-2-butene	**0.70**	**0.68**	**0.70**	**0.71**	**0.71**	**0.73**
1-butene	**1.02**	**1.01**	**1.02**	**1.03**	**1.01**	**1.06**
i-butene	0.64	0.65	0.70	0.62	0.67	0.64
cis-2-butene	**0.86**	**0.85**	**0.82**	**0.85**	**0.85**	**0.87**
2-methyl butane	**2.47**	**2.47**	**2.50**	**2.51**	**2.48**	**2.54**
n-pentane	**1.05**	**1.04**	**1.04**	**1.04**	**1.02**	**1.07**
propyne	0.37	0.38	0.39	0.37	0.38	0.37
1,3-butadiene	**0.99**	**0.97**	**1.00**	**1.01**	**0.96**	**0.98**
trans-2-pentene	**1.28**	**1.31**	**1.29**	**1.30**	**1.29**	**1.32**
1-pentene	**0.40**	**0.37**	**0.42**	**0.38**	**0.39**	**0.39**
cis-pentene	0.52	0.51	0.49	0.51	0.49	0.50
cyclohexane	0.88	0.96	0.91	0.95	0.90	0.98
2-methyl pentane	**0.96**	**0.97**	**0.93**	**0.96**	**0.97**	**0.96**
3-methyl pentane	0.74	0.74	0.75	0.74	0.72	0.79
n-hexane	**1.00**	**1.05**	**1.04**	**1.07**	**1.04**	**1.05**
isoprene	**0.46**	**0.49**	**0.48**	**0.50**	**0.49**	**0.49**
n-heptane	**0.82**	**0.81**	**0.84**	**0.83**	**0.81**	**0.84**
benzene	**1.65**	**1.63**	**1.65**	**1.61**	**1.83**	**1.66**
2,2,4-trimethyl pentane	**0.48**	**0.54**	**0.52**	**0.54**	**0.49**	**0.52**
n-octane	**0.33**	**0.36**	**0.36**	**0.36**	**0.33**	**0.37**
toluene	**2.19**	**2.15**	**2.19**	**2.15**	**2.18**	**2.19**
ethyl-benzene	**0.84**	**0.80**	**0.85**	**0.81**	**0.82**	**0.85**
m+p-xylene	**1.84**	**1.80**	**1.87**	**1.82**	**1.83**	**1.89**
o-xylene	**0.87**	**0.87**	**0.87**	**0.87**	**0.87**	**0.91**
1,3,5-trimethyl benzene	**0.56**	**0.59**	**0.60**	**0.59**	**0.60**	**0.64**
1,2,4-trimethyl benzene	**0.73**	**0.78**	**0.70**	**0.81**	**0.76**	**0.83**
1,2,3-trimethyl benzene	**0.30**	**0.30**	**0.29**	**0.33**	**0.31**	**0.32**

Cylinder ref:	D6 1770		D95 4943		D6 1817	
DATE	**24-May-07**		**25-May-07**	**7-Nov-07**	**29-May-07**	**30-Nov-07**
Component	Amount fraction (nmol/mol)					
ethane	**4.15**	**X**	**4.07**	**4.10**	**4.10**	**4.07**
ethene	**2.00**	**X**	**1.99**	**2.02**	**1.97**	**1.97**
propane	**2.17**	**X**	**2.25**	**2.21**	**2.11**	**2.19**
propene	**1.30**	**X**	**1.30**	**1.24**	**1.27**	**1.25**
iso-butane	**1.98**	**X**	**1.86**	**2.05**	**2.03**	**1.99**
n-butane	**3.91**	**X**	**3.83**	**3.86**	**3.88**	**3.83**
acetylene	**2.82**	**X**	**2.88**	**2.97**	**2.86**	**2.92**
trans-2-butene	**0.70**	**X**	**0.67**	**0.72**	**0.70**	**0.71**
1-butene	**1.04**	**X**	**1.03**	**1.02**	**1.04**	**1.05**
i-butene	0.66	X	0.66	0.64	0.67	0.63
cis-2-butene	**0.89**	**X**	**0.90**	**0.83**	**0.89**	**0.84**
2-methyl butane	**2.53**	**X**	**2.50**	**2.52**	**2.55**	**2.51**
n-pentane	**1.05**	**X**	**1.05**	**1.06**	**1.07**	**1.06**
propyne	0.36	X	0.39	0.37	0.36	0.36
1,3-butadiene	**0.97**	**X**	**1.00**	**0.97**	**1.02**	**0.97**
trans-2-pentene	**1.30**	**X**	**1.27**	**1.30**	**1.31**	**1.31**
1-pentene	**0.41**	**X**	**0.40**	**0.37**	**0.39**	**0.38**
cis-pentene	0.52	X	0.49	0.51	0.51	0.51
cyclohexane	0.92	X	0.92	0.96	0.94	0.95
2-methyl pentane	**0.98**	**X**	**0.96**	**1.00**	**0.97**	**0.95**
3-methyl pentane	0.69	X	0.79	0.70	0.71	0.78
n-hexane	**1.03**	**X**	**1.04**	**1.05**	**1.05**	**1.05**
isoprene	**0.50**	**X**	**0.50**	**0.47**	**0.48**	**0.50**
n-heptane	**0.83**	**X**	**0.82**	**0.85**	**0.85**	**0.83**
benzene	**1.66**	**X**	**1.65**	**1.64**	**1.69**	**1.66**
2,2,4-trimethyl pentane	**0.52**	**X**	**0.47**	**0.53**	**0.50**	**0.53**
n-octane	**0.35**	**X**	**0.34**	**0.38**	**0.33**	**0.36**
toluene	**2.19**	**X**	**2.23**	**2.22**	**2.23**	**2.18**
ethyl-benzene	**0.90**	**X**	**0.80**	**0.84**	**0.87**	**0.84**
m+p-xylene	**1.95**	**X**	**1.81**	**1.85**	**1.89**	**1.85**
o-xylene	**0.86**	**X**	**0.86**	**0.88**	**0.86**	**0.90**
1,3,5-trimethyl benzene	**0.65**	**X**	**0.60**	**0.60**	**0.61**	**0.63**
1,2,4-trimethyl benzene	**0.82**	**X**	**0.75**	**0.84**	**0.76**	**0.84**
1,2,3-trimethyl benzene	**0.28**	**X**	**0.29**	**0.30**	**0.26**	**0.32**

Cylinder ref:	D6 1769		D6 1818		D6 1697	
DATE	**31-May-07**	**26-Oct-07**	**4-Jun-07**	**5-Nov-07**	**5-Jun-07**	**25-Oct-07**
Component	Amount fraction (nmol/mol)					
ethane	**4.05**	**4.06**	**4.11**	**4.13**	**4.05**	**4.10**
ethene	**2.00**	**2.00**	**2.01**	**1.98**	**1.98**	**1.98**
propane	**2.25**	**2.19**	**2.26**	**2.22**	**2.18**	**2.12**
propene	**1.29**	**1.25**	**1.26**	**1.28**	**1.28**	**1.27**
iso-butane	**2.01**	**2.01**	**1.99**	**2.06**	**2.13**	**1.98**
n-butane	**3.89**	**3.89**	**3.92**	**3.89**	**3.87**	**3.76**
acetylene	**2.80**	**2.88**	**2.80**	**2.94**	**2.77**	**2.85**
trans-2-butene	**0.70**	**0.72**	**0.72**	**0.71**	**0.75**	**0.71**
1-butene	**1.04**	**1.01**	**1.06**	**1.01**	**1.04**	**1.04**
i-butene	0.66	0.63	0.67	0.63	0.67	0.65
cis-2-butene	**0.85**	**0.87**	**0.88**	**0.85**	**0.85**	**0.85**
2-methyl butane	**2.50**	**2.47**	**2.50**	**2.51**	**2.53**	**2.53**
n-pentane	**1.04**	**1.07**	**1.07**	**1.03**	**1.15**	**1.05**
propyne	0.39	0.37	0.39	0.38	0.37	0.39
1,3-butadiene	**0.99**	**0.98**	**0.99**	**0.97**	**1.01**	**1.02**
trans-2-pentene	**1.33**	**1.33**	**1.33**	**1.31**	**1.26**	**1.32**
1-pentene	**0.38**	**0.38**	**0.38**	**0.37**	**0.39**	**0.39**
cis-pentene	0.49	0.51	0.51	0.50	0.49	0.52
cyclohexane	0.87	0.96	0.89	0.96	0.88	0.96
2-methyl pentane	**0.96**	**0.94**	**0.95**	**0.93**	**0.93**	**0.97**
3-methyl pentane	0.72	0.77	0.72	0.80	0.71	0.73
n-hexane	**1.02**	**1.05**	**1.06**	**1.04**	**1.02**	**1.06**
isoprene	**0.48**	**0.48**	**0.47**	**0.50**	**0.48**	**0.48**
n-heptane	**0.84**	**0.83**	**0.87**	**0.85**	**0.82**	**0.83**
benzene	**1.67**	**1.67**	**1.70**	**1.65**	**1.66**	**1.55**
2,2,4-trimethyl pentane	**0.50**	**0.49**	**0.49**	**0.54**	**0.49**	**0.51**
n-octane	**0.36**	**0.38**	**0.33**	**0.39**	**0.35**	**0.37**
toluene	**2.22**	**2.20**	**2.23**	**2.19**	**2.25**	**2.21**
ethyl-benzene	**0.88**	**0.86**	**0.90**	**0.83**	**0.89**	**0.85**
m+p-xylene	**1.94**	**1.90**	**1.90**	**1.86**	**1.94**	**1.89**
o-xylene	**0.90**	**0.89**	**0.92**	**0.89**	**0.90**	**0.91**
1,3,5-trimethyl benzene	**0.62**	**0.62**	**0.63**	**0.59**	**0.60**	**0.61**
1,2,4-trimethyl benzene	**0.80**	**0.82**	**0.79**	**0.83**	**0.84**	**0.82**
1,2,3-trimethyl benzene	**0.30**	**0.32**	**0.31**	**0.33**	**0.27**	**0.32**

Cylinder ref:	D6 1848		D6 1677		D6 1780	
DATE	**6-Jun-07**	**6-Nov-07**	**7-Jun-07**	**19-Nov-07**	**8-Jun-07**	**14-Nov-07**
Component	Amount fraction (nmol/mol)					
ethane	**4.08**	**4.09**	**4.10**	**4.10**	**4.07**	**4.07**
ethene	**1.99**	**1.96**	**1.97**	**1.95**	**1.96**	**1.97**
propane	**2.19**	**2.23**	**2.21**	**2.19**	**2.24**	**2.19**
propene	**1.30**	**1.24**	**1.32**	**1.30**	**1.32**	**1.24**
iso-butane	**1.96**	**1.97**	**1.93**	**1.98**	**2.13**	**2.01**
n-butane	**3.82**	**3.82**	**3.87**	**3.88**	**3.85**	**3.92**
acetylene	**2.86**	**2.77**	**2.81**	**3.01**	**2.82**	**2.98**
trans-2-butene	**0.72**	**0.71**	**0.69**	**0.72**	**0.69**	**0.71**
1-butene	**1.06**	**1.03**	**1.01**	**1.05**	**0.98**	**1.06**
i-butene	0.64	0.65	0.65	0.64	0.64	0.62
cis-2-butene	**0.85**	**0.85**	**0.84**	**0.86**	**0.85**	**0.85**
2-methyl butane	**2.50**	**2.53**	**2.50**	**2.53**	**2.49**	**2.49**
n-pentane	**1.05**	**1.04**	**1.04**	**1.09**	**1.06**	**1.09**
propyne	0.39	0.38	0.37	0.39	0.39	0.40
1,3-butadiene	**0.99**	**0.97**	**0.98**	**1.01**	**0.98**	**1.00**
trans-2-pentene	**1.30**	**1.30**	**1.31**	**1.30**	**1.29**	**1.29**
1-pentene	**0.37**	**0.37**	**0.36**	**0.39**	**0.36**	**0.37**
cis-pentene	0.49	0.51	0.47	0.52	0.49	0.53
cyclohexane	0.94	0.96	0.92	0.96	0.91	0.97
2-methyl pentane	**0.97**	**0.94**	**0.97**	**0.99**	**0.99**	**0.96**
3-methyl pentane	0.74	0.74	0.75	0.75	0.72	0.76
n-hexane	**1.02**	**1.03**	**1.04**	**1.04**	**1.05**	**1.06**
isoprene	**0.46**	**0.48**	**0.47**	**0.49**	**0.47**	**0.48**
n-heptane	**0.85**	**0.83**	**0.82**	**0.84**	**0.82**	**0.84**
benzene	**1.67**	**1.62**	**1.67**	**1.62**	**1.69**	**1.61**
2,2,4-trimethyl pentane	**0.50**	**0.53**	**0.48**	**0.52**	**0.52**	**0.50**
n-octane	**0.33**	**0.37**	**0.31**	**0.37**	**0.34**	**0.35**
toluene	**2.21**	**2.21**	**2.23**	**2.18**	**2.21**	**2.16**
ethyl-benzene	**0.85**	**0.85**	**0.88**	**0.83**	**0.87**	**0.82**
m+p-xylene	**1.90**	**1.88**	**1.93**	**1.85**	**1.94**	**1.85**
o-xylene	**0.89**	**0.90**	**0.89**	**0.91**	**0.91**	**0.88**
1,3,5-trimethyl benzene	**0.62**	**0.62**	**0.61**	**0.60**	**0.64**	**0.60**
1,2,4-trimethyl benzene	**0.78**	**0.87**	**0.81**	**0.82**	**0.79**	**0.80**
1,2,3-trimethyl benzene	**0.27**	**0.32**	**0.28**	**0.35**	**0.30**	**0.33**

Cylinder ref:	D6 1767		D6 1775	
DATE	**19-Jun-07**	**13-Nov-07**	**21-Jun-07**	**8-Nov-07**
Component	Amount fraction (nmol/mol)			
ethane	**4.13**	**4.04**	**4.08**	**4.04**
ethene	**2.01**	**1.91**	**2.01**	**1.92**
propane	**2.24**	**2.18**	**2.25**	**2.20**
propene	**1.27**	**1.25**	**1.29**	**1.30**
iso-butane	**2.09**	**2.01**	**2.04**	**2.06**
n-butane	**3.92**	**3.83**	**3.83**	**3.81**
acetylene	**2.93**	**2.91**	**2.79**	**2.95**
trans-2-butene	**0.73**	**0.69**	**0.69**	**0.71**
1-butene	**1.06**	**1.01**	**1.03**	**1.03**
i-butene	0.68	0.64	0.62	0.65
cis-2-butene	**0.84**	**0.88**	**0.87**	**0.85**
2-methyl butane	**2.54**	**2.55**	**2.46**	**2.55**
n-pentane	**1.03**	**1.07**	**1.04**	**1.09**
propyne	0.36	0.37	0.38	0.39
1,3-butadiene	**0.97**	**0.95**	**0.95**	**0.99**
trans-2-pentene	**1.30**	**1.31**	**1.27**	**1.30**
1-pentene	**0.39**	**0.38**	**0.37**	**0.38**
cis-pentene	0.49	0.51	0.49	0.51
cyclohexane	0.98	0.94	0.91	0.98
2-methyl pentane	**0.98**	**0.98**	**0.95**	**0.99**
3-methyl pentane	0.77	0.73	0.72	0.75
n-hexane	**1.08**	**1.07**	**1.04**	**1.07**
isoprene	**0.51**	**0.49**	**0.48**	**0.48**
n-heptane	**0.84**	**0.85**	**0.85**	**0.83**
benzene	**1.75**	**1.60**	**1.69**	**1.65**
2,2,4-trimethyl pentane	**0.53**	**0.52**	**0.49**	**0.50**
n-octane	**0.37**	**0.36**	**0.37**	**0.35**
toluene	**2.19**	**2.17**	**2.21**	**2.20**
ethyl-benzene	**0.87**	**0.82**	**0.86**	**0.81**
m+p-xylene	**1.90**	**1.83**	**1.91**	**1.83**
o-xylene	**0.91**	**0.88**	**0.89**	**0.89**
1,3,5-trimethyl benzene	**0.63**	**0.58**	**0.63**	**0.62**
1,2,4-trimethyl benzene	**0.80**	**0.82**	**0.83**	**0.76**
1,2,3-trimethyl benzene	**0.31**	**0.31**	**0.28**	**0.31**

Annex C: Cylinder allocation and despatch

Laboratory	Cylinders	Despatch		Return	
		Date	Pressure (bar)	Date	Pressure (bar)
ERLAP	D95 4790 D6 1849	09-May-07 25-May-07	99 22.5	23-Jul-07 23-Jul-07	44.1 13.6
NPL	D95 4804 D6 1773	n/a	n/a	n/a	n/a
VMM	D95 4934 D8 1848	12-Jun-07	102 22.6	21-Aug-07	68 11
AOL-UUW	D83 8784 D6 1770	11-Jun-07	102 22.7	31-Jul-07	0 0
FMI	D83 8781 D95 4943	11-Jun-07	102 22.7	20-Jul-07	87 6.5
UBA (A)	D95 4965 D6 1818	11-Jun-07	102 22.7	31-Jul-07	65 15
ISSeP	D95 4944 D6 1769	11-Jun-07	102 22.7	06-Sep-07	79 17
CHMI	D95 4775 D6 1815	25-May-07	101 22.5	25-Feb-08	90 19.2
AEAT	D95 4932 D6 1697	12-Jun-07	101 22.6	06-Sep-07	94 20
Inst do Amb	D83 8930 D6 1748	12-Jun-07	102 22.5	17-Dec-07	90.5 18.2
EMD	D95 4968 D6 1767	22-Jun-07	102 22.6	17-Sep-07	81 16
EPA	D95 4936 D6 1804	25-May-07	102 22.5	19-Sep-07	79.2 18.6
ISCIII	D95 4945 D6 1780	12-Jun-07	103 22.6	10-Oct-07	101.7 22.7
EMPA	D95 4947 D6 1677	12-Jun-07	101 22.7	31-Jul-07	99 21
EARS	D83 8907 D95 4770	25-May-07	104 22.5	28-Aug-07	93 19.1
IVL	D95 4937 D6 1775	22-Jun-07	103 22.6	01-Oct-07	101.4 21.2
CNR	D95 4778 D6 1817	11-Jun-07	101.5 22.7	31-Jul-07	101 15
NERI	D29 2405	02-Jul-07	101	28-Jan-08	92

Annex D: Uncertainty estimates

A measurement of a participant standard consisted of 2 analyses of the participant standard and 3 analyses of the working standard in the sequence A-B-A-B-A.

The uncertainty assigned to a result is calculated by evaluating the standard deviation of the sample across the 3 rounds of measurements for the synthetic and the 2 rounds of measurements for the ambient standards. This was achieved by averaging the relative variances calculated from each round of each version and then taking the square root. This estimate for the measurement uncertainty was used in calculating the expanded uncertainty for the drift parameter.

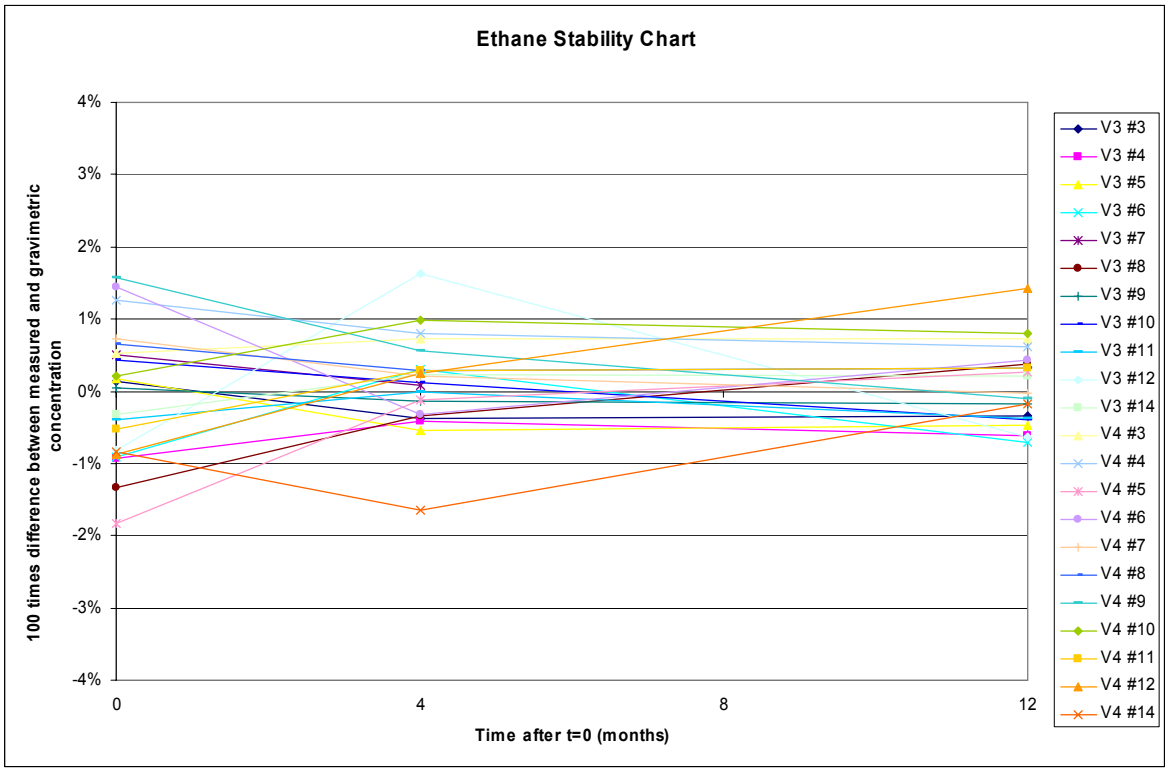
Synthetic

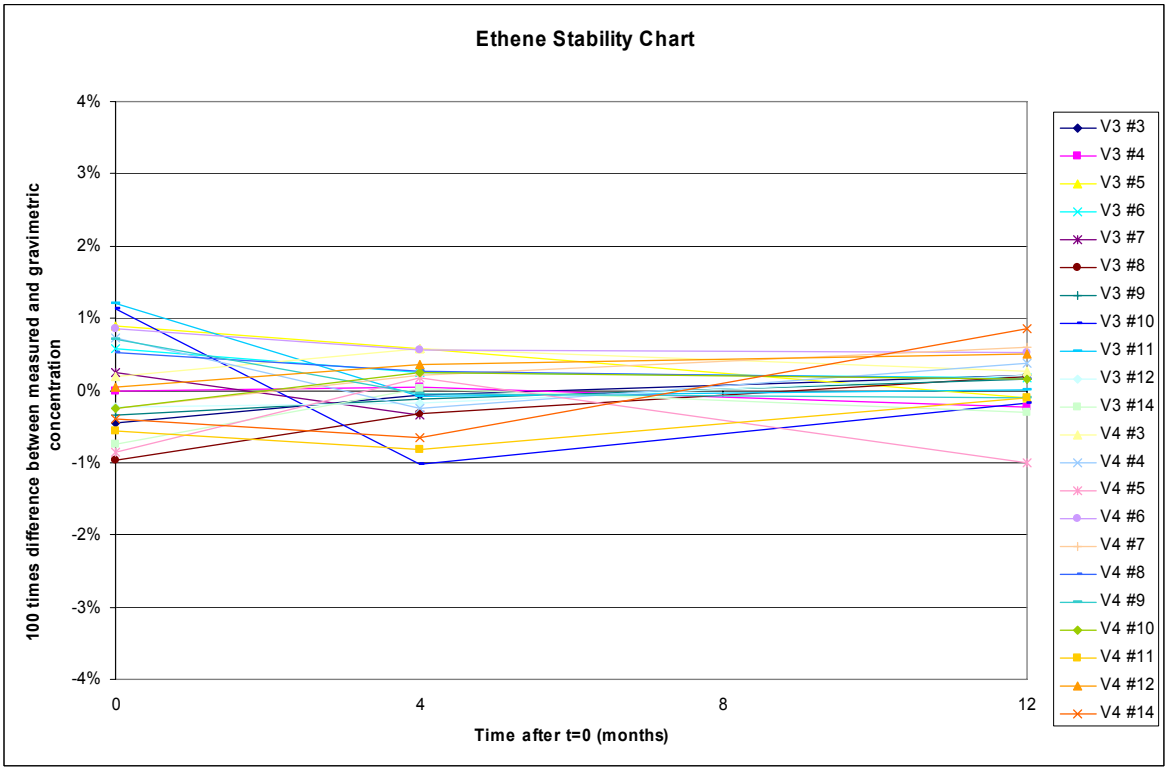
	VARIANCE of measured concentration difference from gravimetric value							
	Round 1		Round 2		Round 3			
	v4	v3	v4	v3	v4	v3	AVG	u_{prec}
ethane	1.20E-04	3.81E-05	5.18E-05	3.51E-05	2.14E-05	1.27E-05	4.66E-05	**0.68%**
ethene	3.37E-05	5.62E-05	2.11E-05	1.59E-05	2.43E-05	4.04E-06	2.59E-05	**0.51%**
propane	7.55E-05	8.19E-05	1.37E-05	2.16E-05	2.87E-05	3.05E-05	4.20E-05	**0.65%**
propene	1.06E-04	6.46E-05	1.04E-04	1.20E-04	1.34E-04	9.12E-05	1.03E-04	**1.02%**
iso-butane	3.54E-05	1.44E-04	7.36E-05	1.28E-04	1.97E-04	1.55E-04	1.22E-04	**1.11%**
n-butane	5.71E-05	5.93E-05	1.67E-05	6.09E-05	6.22E-05	9.76E-05	5.90E-05	**0.77%**
acetylene	2.88E-05	9.10E-05	9.35E-05	6.13E-05	9.42E-05	8.28E-05	7.53E-05	**0.87%**
trans-2-butene	2.75E-05	2.01E-05	2.68E-05	7.42E-06	5.75E-05	9.29E-06	2.48E-05	**0.50%**
1-butene	3.84E-05	1.44E-05	2.97E-05	5.52E-05	8.61E-05	4.44E-05	4.47E-05	**0.67%**
cis-2-butene	3.62E-05	1.10E-04	5.58E-05	2.01E-05	1.27E-04	6.40E-05	6.90E-05	**0.83%**
2-methyl butane	2.93E-05	3.31E-05	7.69E-05	4.76E-05	3.71E-05	1.17E-04	5.69E-05	**0.75%**
n-pentane	4.21E-05	6.65E-05	6.40E-05	3.35E-05	6.10E-05	8.04E-05	5.79E-05	**0.76%**
1,3-butadiene	3.50E-05	2.25E-05	3.46E-05	1.83E-05	6.50E-05	5.87E-05	3.90E-05	**0.62%**
trans-2-pentene	1.65E-05	5.25E-05	2.60E-05	5.81E-05	4.43E-05	5.94E-05	4.28E-05	**0.65%**
1-pentene	1.56E-05	8.92E-05	2.28E-05	9.41E-06	7.63E-05	8.27E-05	4.93E-05	**0.70%**
2-methyl pentane	2.95E-05	6.48E-05	6.79E-05	3.34E-05	8.14E-05	7.86E-05	5.92E-05	**0.77%**
n-hexane	2.43E-05	5.08E-05	1.80E-05	2.00E-05	3.88E-05	4.98E-05	3.36E-05	**0.58%**
isoprene	4.84E-05	3.39E-05	3.48E-05	3.73E-05	4.09E-05	1.71E-05	3.54E-05	**0.59%**
n-heptane	3.24E-05	4.19E-05	7.15E-06	2.78E-05	7.26E-05	6.14E-05	4.05E-05	**0.64%**
benzene	2.35E-05	2.24E-05	3.70E-05	1.64E-05	4.55E-05	5.22E-05	3.28E-05	**0.57%**
2,2,4-trimethyl pentane	4.86E-05	5.77E-05	2.23E-05	3.09E-05	7.01E-05	1.00E-04	5.49E-05	**0.74%**
n-octane	3.39E-05	3.34E-05	1.85E-05	4.63E-05	5.57E-05	6.07E-05	4.14E-05	**0.64%**
toluene	4.64E-05	5.74E-05	4.42E-05	5.59E-05	1.29E-04	1.07E-04	7.34E-05	**0.86%**
ethyl-benzene	6.38E-05	6.13E-05	4.64E-05	3.83E-05	4.97E-05	9.75E-06	4.49E-05	**0.67%**
m+p-xylene	4.38E-05	5.17E-05	5.77E-05	5.15E-05	5.95E-05	2.75E-05	4.86E-05	**0.70%**
o-xylene	5.66E-05	1.10E-04	3.71E-05	4.47E-05	4.42E-05	4.97E-05	5.70E-05	**0.76%**
1,3,5-trimethyl benzene	1.24E-04	2.01E-04	6.56E-05	8.40E-05	9.45E-05	6.56E-05	1.06E-04	**1.03%**
1,2,4-trimethyl benzene	7.93E-05	2.03E-04	7.45E-05	9.27E-05	5.02E-05	9.62E-05	9.93E-05	**1.00%**
1,2,3-trimethyl benzene	1.32E-04	1.63E-04	1.30E-04	1.10E-04	1.41E-04	2.45E-04	1.53E-04	**1.24%**

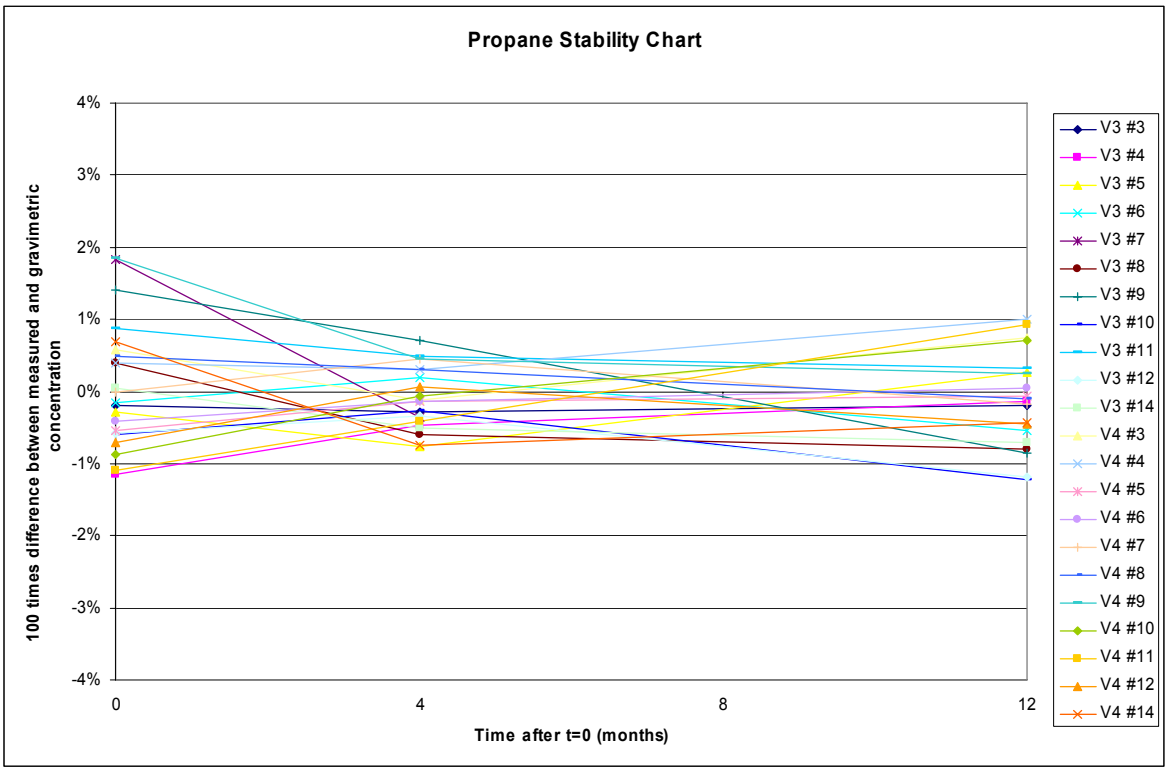
Ambient

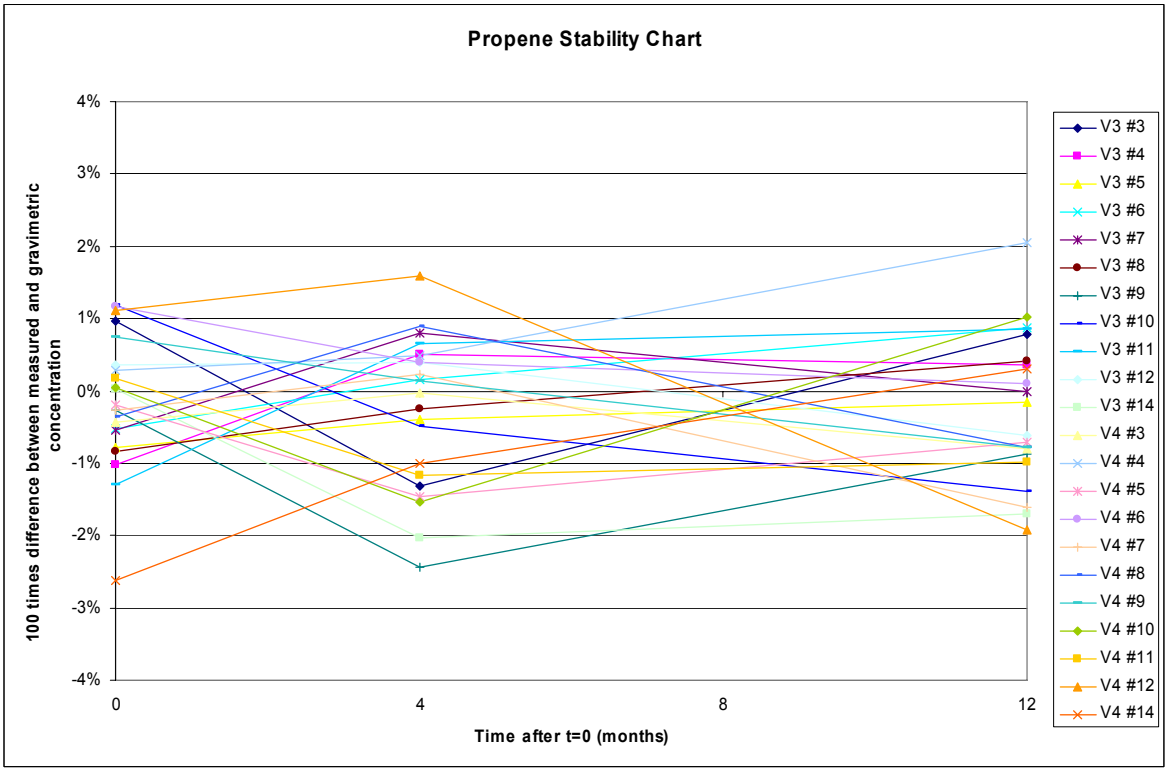
	VARIANCE of measured concentration difference from mean value			
	Round 1	Round 2	AVG	u_{prec}
ethane	8.03E-05	3.92E-05	5.98E-05	**0.77%**
ethene	5.32E-04	3.14E-04	4.23E-04	**2.06%**
propane	3.24E-04	1.28E-04	2.26E-04	**1.50%**
propene	9.47E-04	2.61E-04	6.04E-04	**2.46%**
iso-butane	1.44E-03	2.50E-04	8.47E-04	**2.91%**
n-butane	9.33E-05	1.01E-04	9.71E-05	**0.99%**
acetylene	4.02E-04	7.18E-04	5.60E-04	**2.37%**
Trans-2-butene	7.00E-04	3.81E-04	5.40E-04	**2.32%**
1-butene	4.75E-04	2.96E-04	3.86E-04	**1.96%**
i-butene	8.59E-04	4.81E-04	6.70E-04	**2.59%**
cis-2-butene	6.81E-04	2.52E-04	4.66E-04	**2.16%**
2-methyl butane	1.06E-04	1.19E-04	1.13E-04	**1.06%**
n-pentane	9.37E-04	2.85E-04	6.11E-04	**2.47%**
propyne	1.52E-03	7.78E-04	1.15E-03	**3.39%**
1,3-butadiene	3.96E-04	4.62E-04	4.29E-04	**2.07%**
Trans-2-pentene	1.95E-04	7.16E-05	1.33E-04	**1.15%**
1-pentene	1.68E-03	4.84E-04	1.08E-03	**3.29%**
cis-pentene	6.91E-04	2.56E-04	4.73E-04	**2.18%**
cyclohexane	1.06E-03	1.03E-04	5.82E-04	**2.41%**
2-methyl pentane	6.52E-04	8.44E-04	7.48E-04	**2.74%**
3-methyl pentane	1.34E-03	1.10E-03	1.22E-03	**3.50%**
n-hexane	3.08E-04	1.69E-04	2.38E-04	**1.54%**
isoprene	1.02E-03	4.17E-04	7.21E-04	**2.68%**
n-heptane	3.96E-04	1.69E-04	2.82E-04	**1.68%**
benzene	7.11E-04	3.31E-04	5.21E-04	**2.28%**
2,2,4-trimethyl pentane	1.04E-03	7.27E-04	8.85E-04	**2.97%**
n-octane	2.41E-03	1.15E-03	1.78E-03	**4.22%**
toluene	7.20E-05	1.39E-04	1.05E-04	**1.03%**
Ethyl-benzene	9.07E-04	4.02E-04	6.54E-04	**2.56%**
m+p-xylene	6.38E-04	2.29E-04	4.34E-04	**2.08%**
o-xylene	5.07E-04	2.99E-04	4.03E-04	**2.01%**
1,3,5-trimethyl benzene	1.77E-03	8.56E-04	1.31E-03	**3.62%**
1,2,4-trimethyl benzene	3.10E-03	1.21E-03	2.16E-03	**4.64%**
1,2,3-trimethyl benzene	2.88E-03	1.93E-03	2.40E-03	**4.90%**

Annex E: Individual component stability charts






Propane Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


Propene Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
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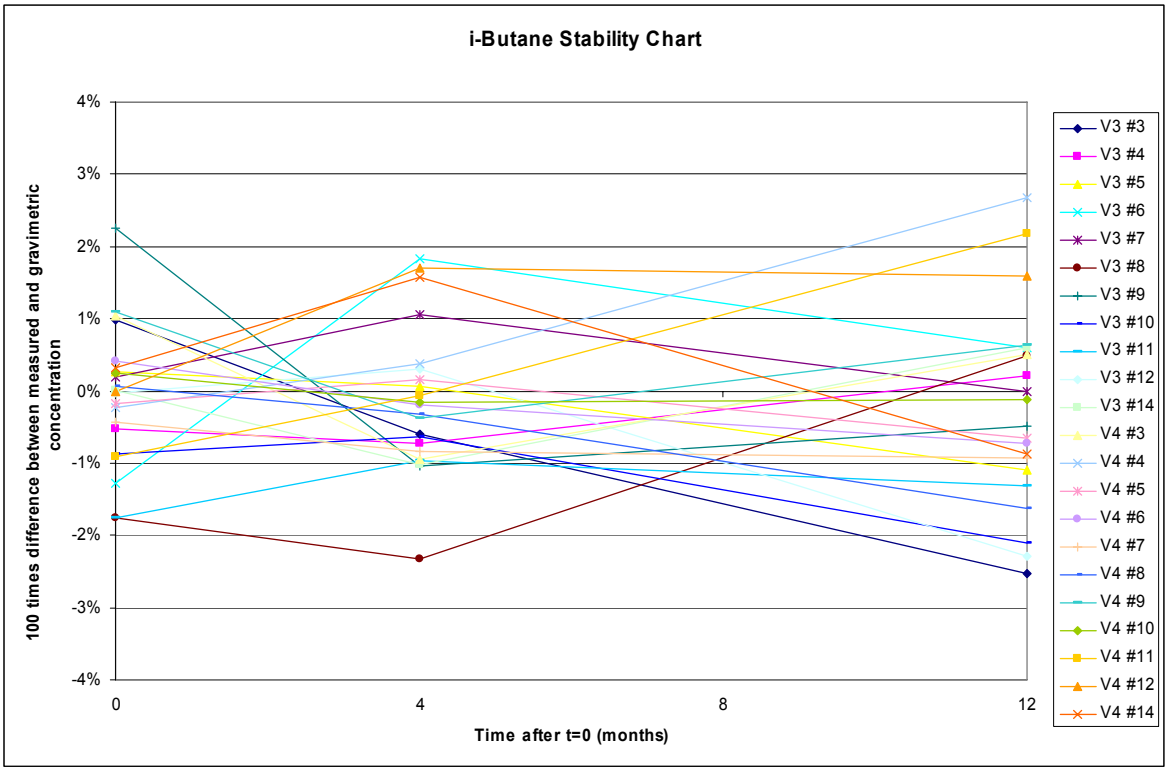
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


i-Butane Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
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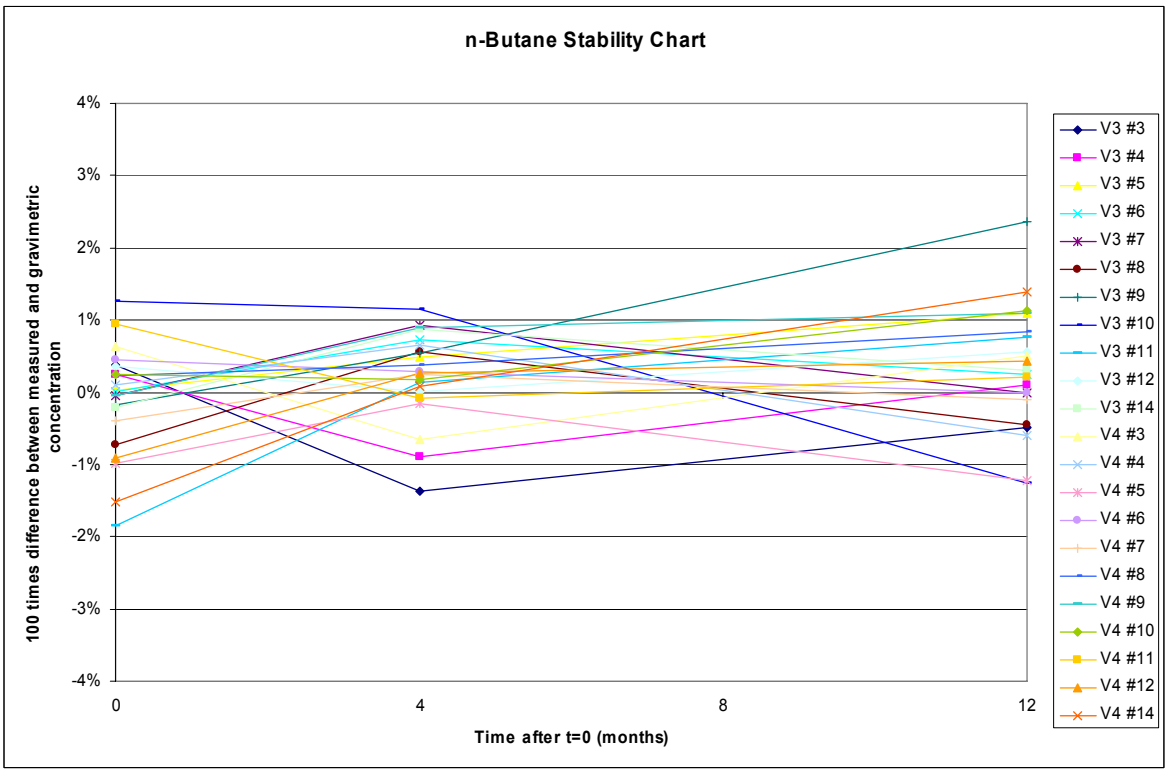
V4 #10
V4 #11
V4 #12
V4 #14


n-Butane Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
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V4 #7
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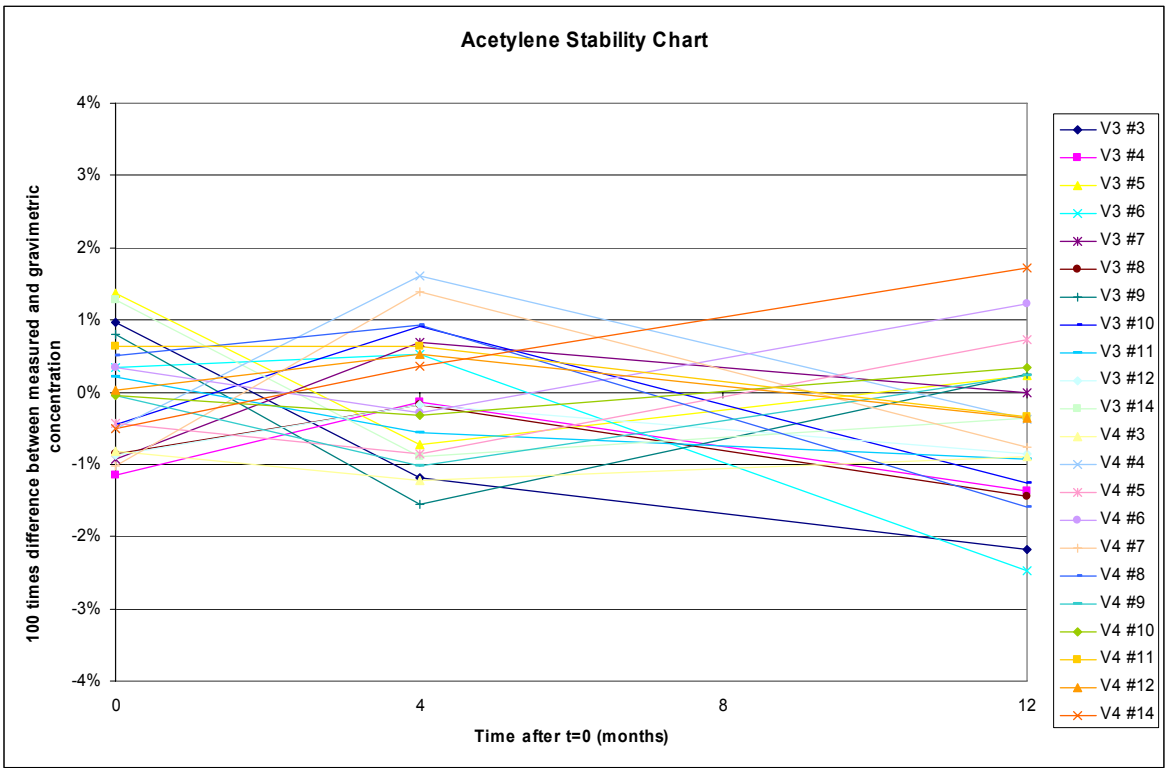
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


Acetylene Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
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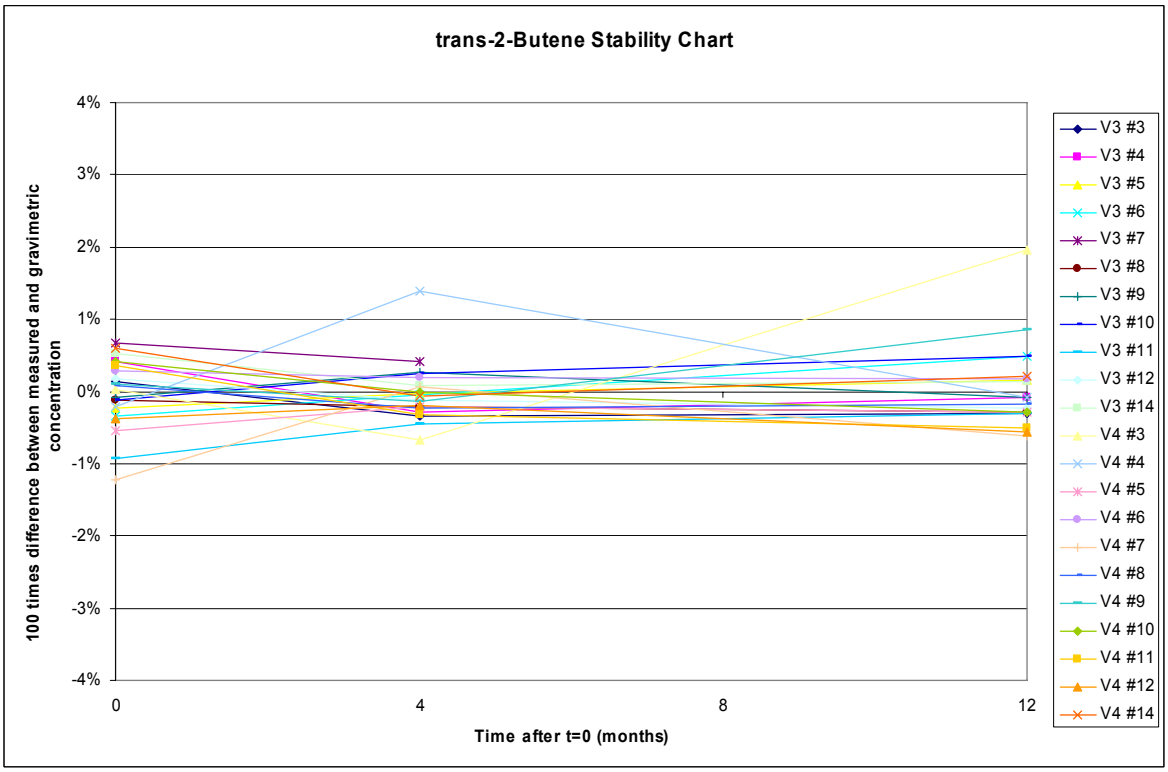
V4 #11
V4 #12
V4 #14


trans-2-Butene Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
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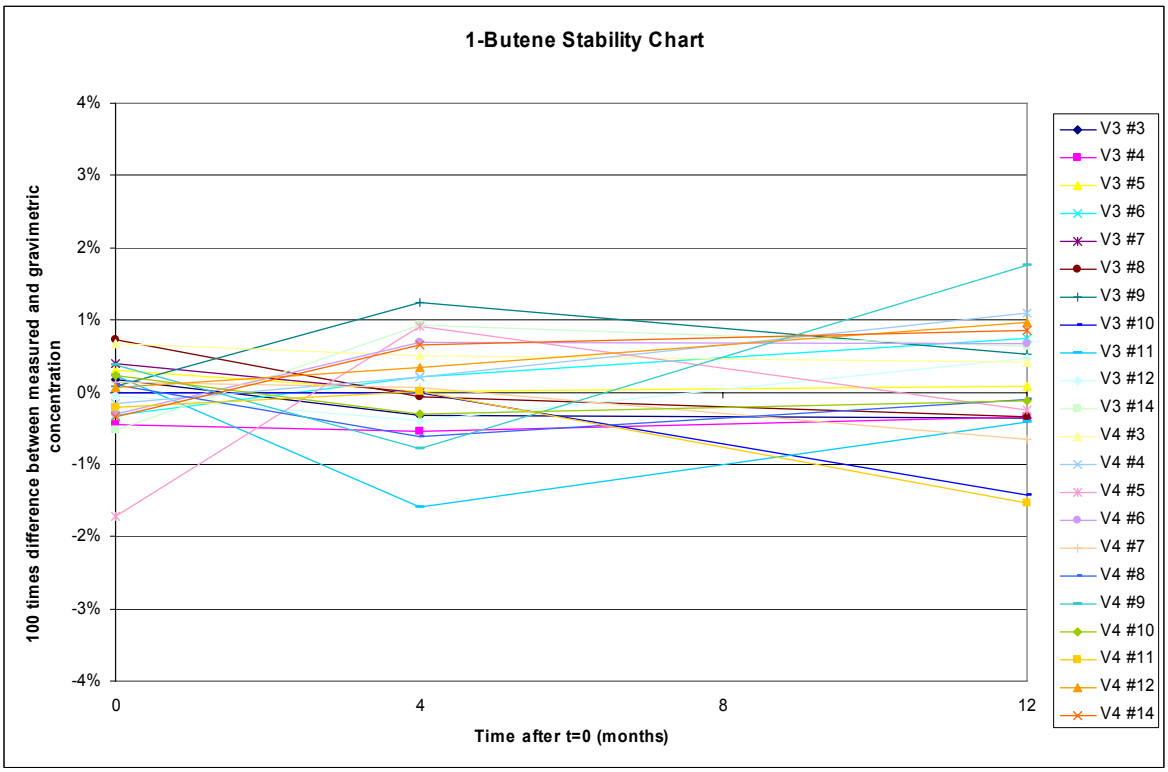
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


1-Butene Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
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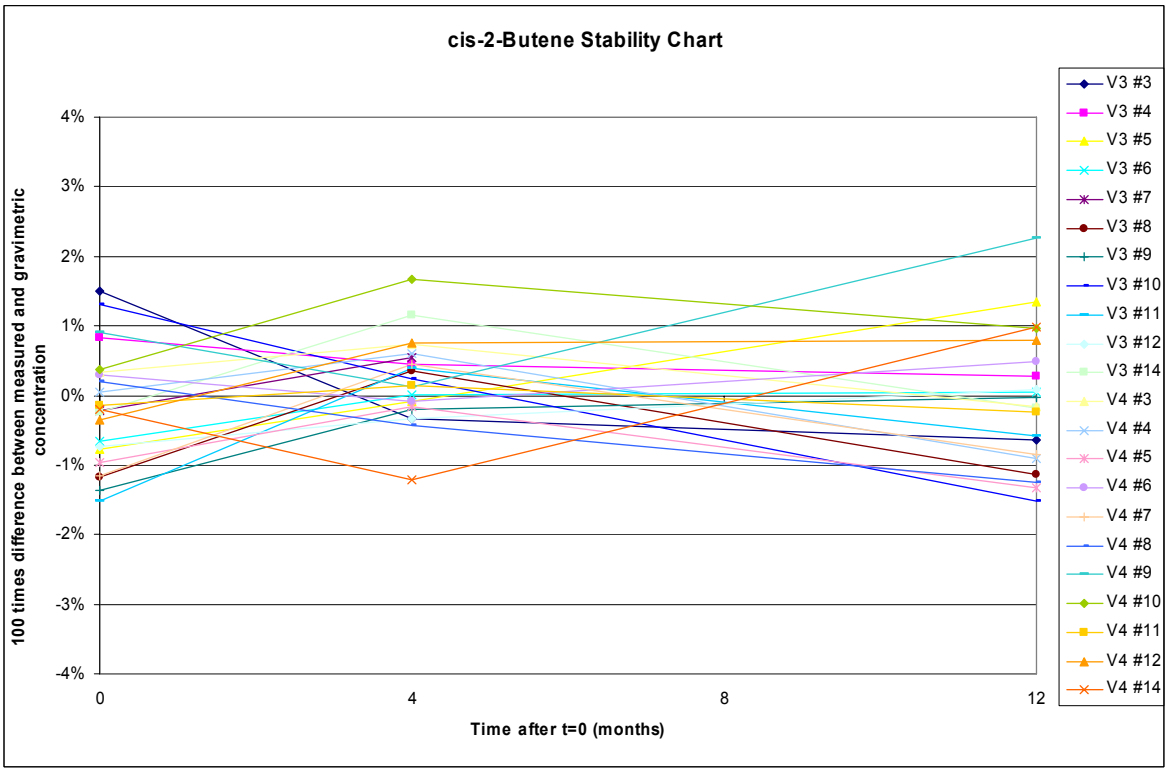
V4 #12
V4 #14


cis-2-Butene Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
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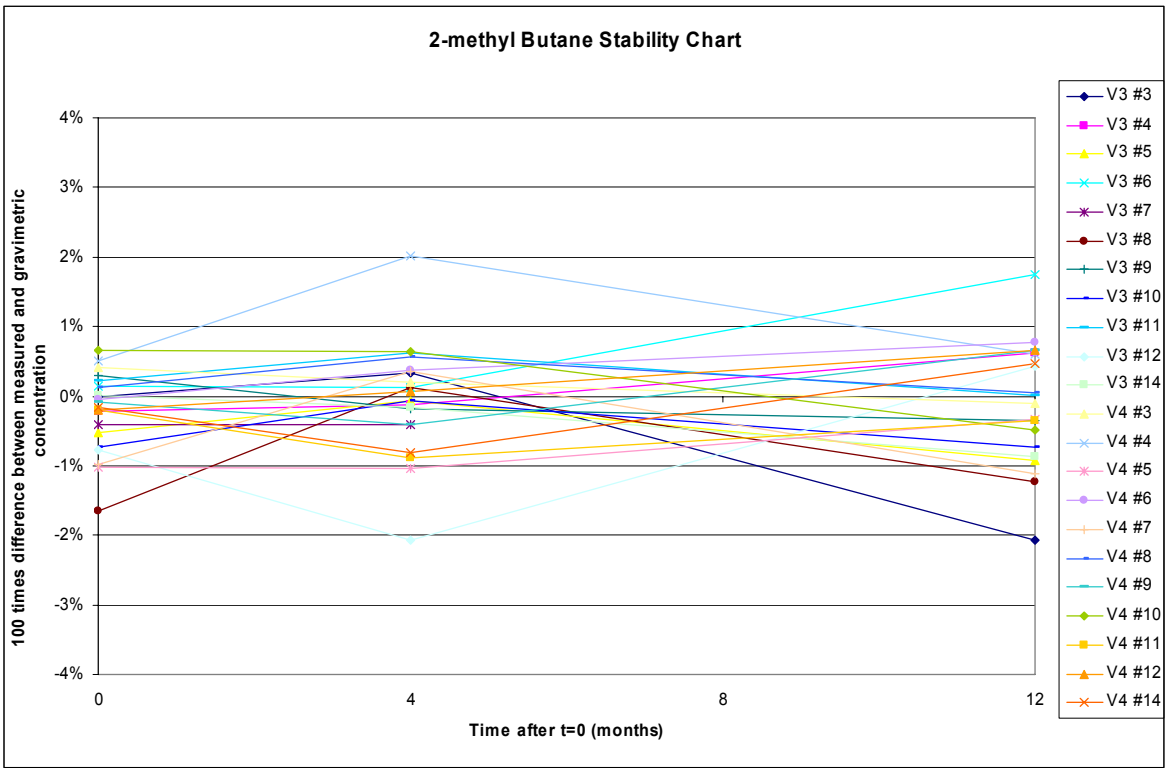
V4 #12
V4 #14


2-methyl Butane Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
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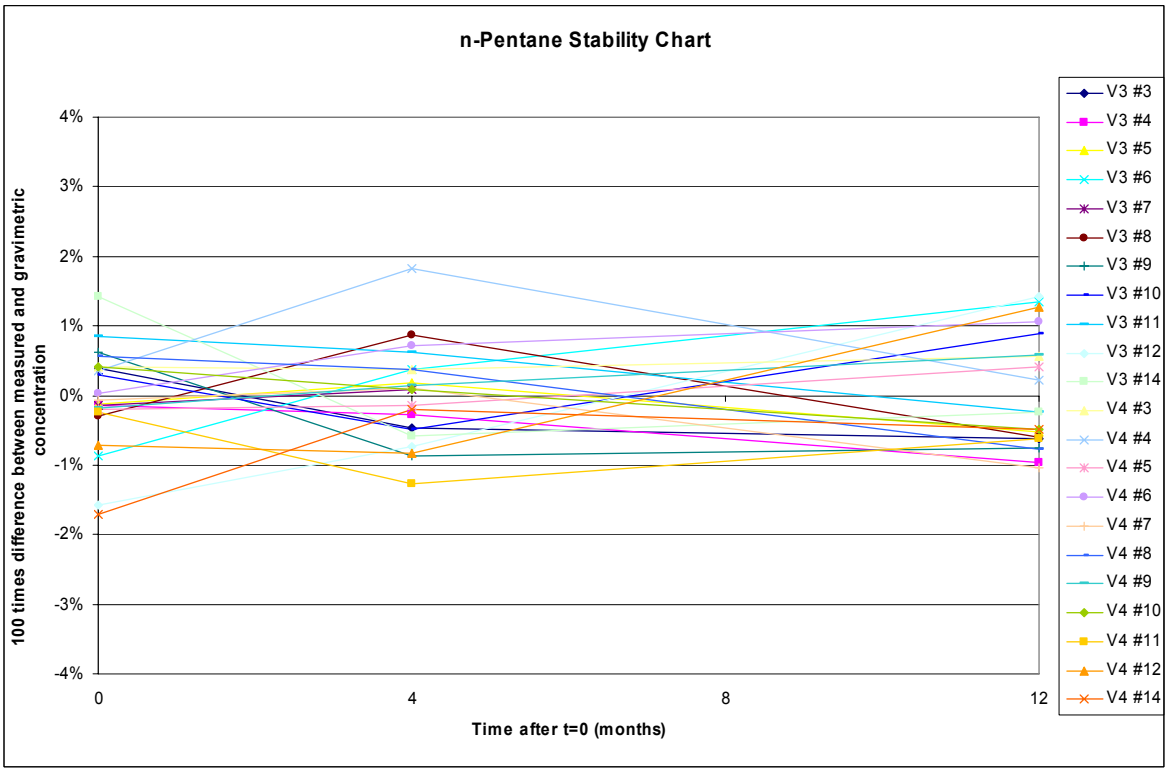
V4 #12
V4 #14


n-Pentane Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
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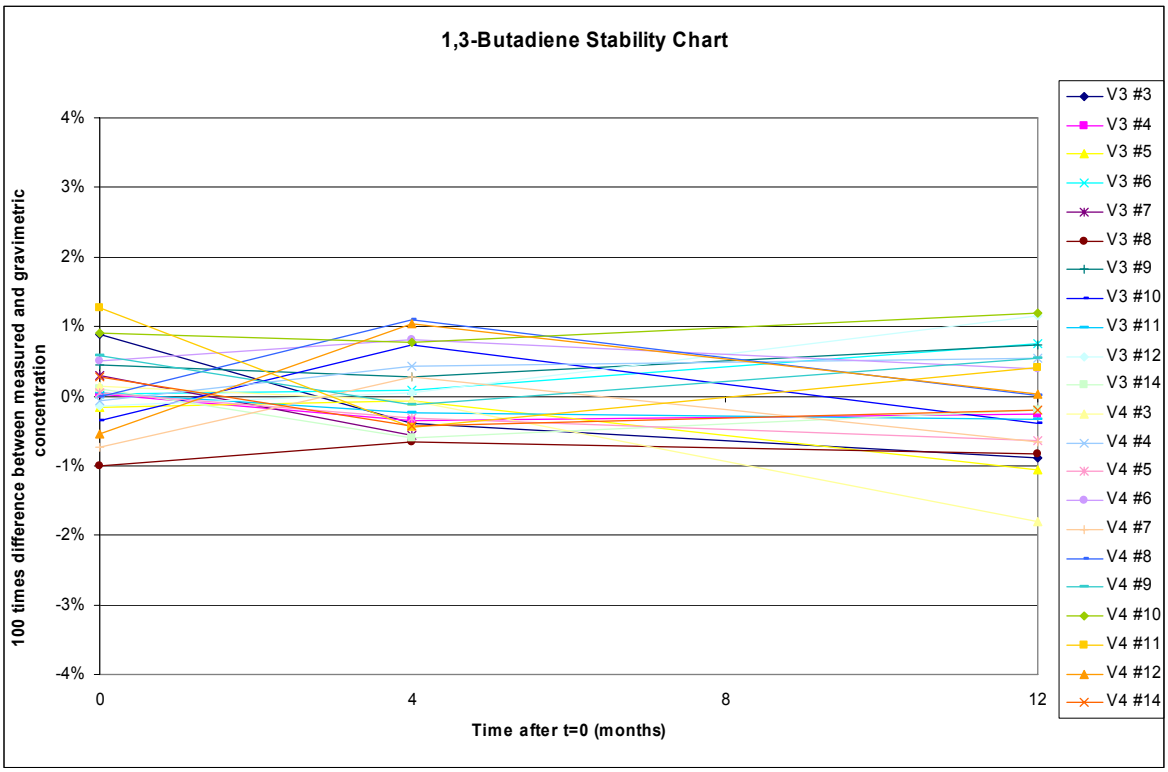
V4 #12
V4 #14


1,3-Butadiene Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
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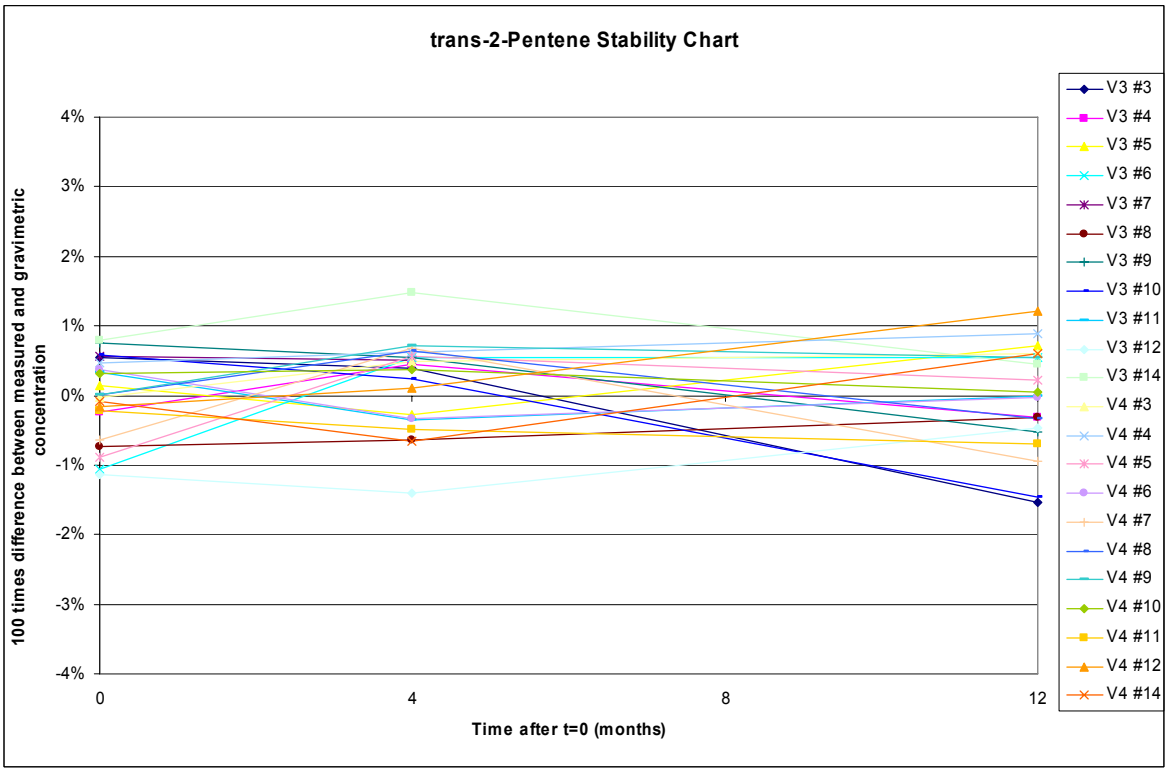
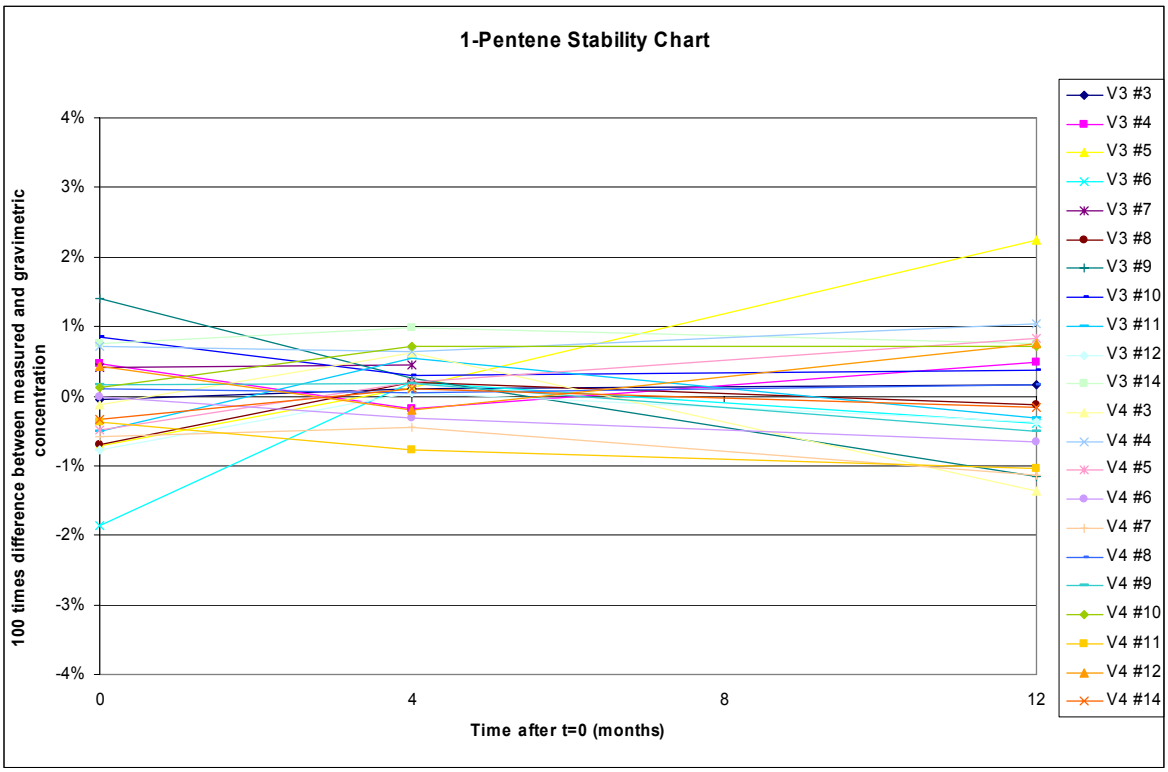
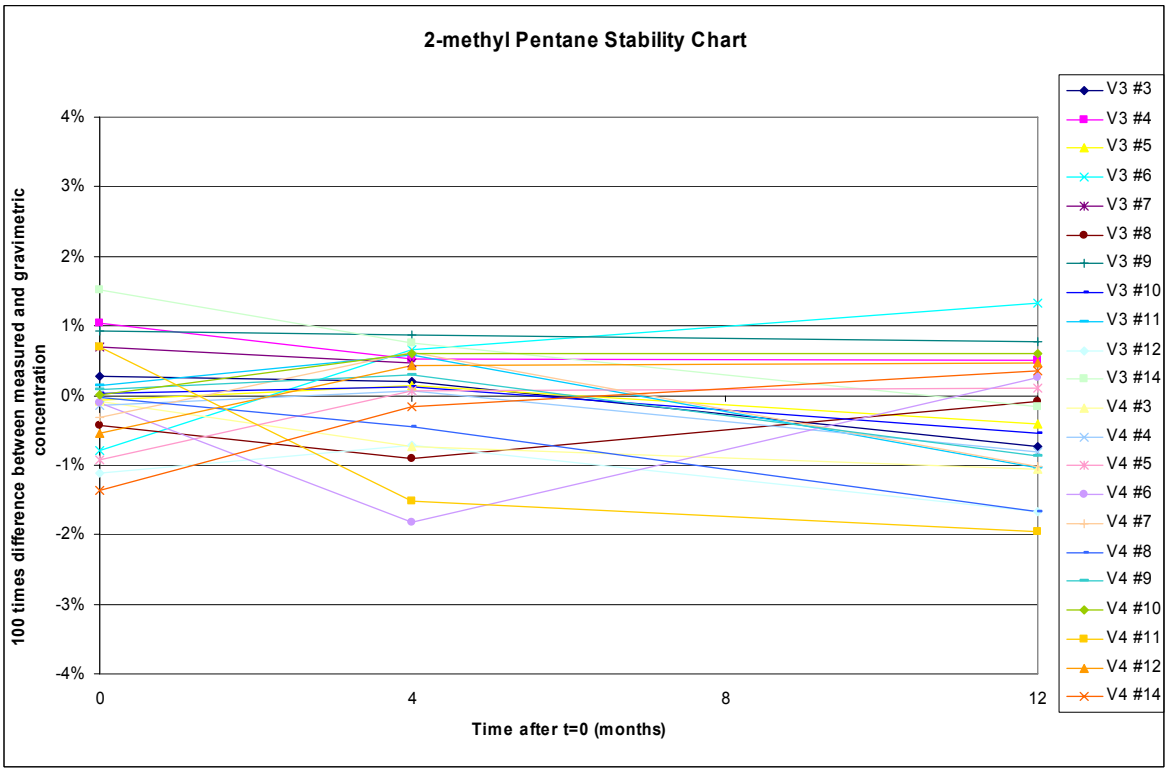
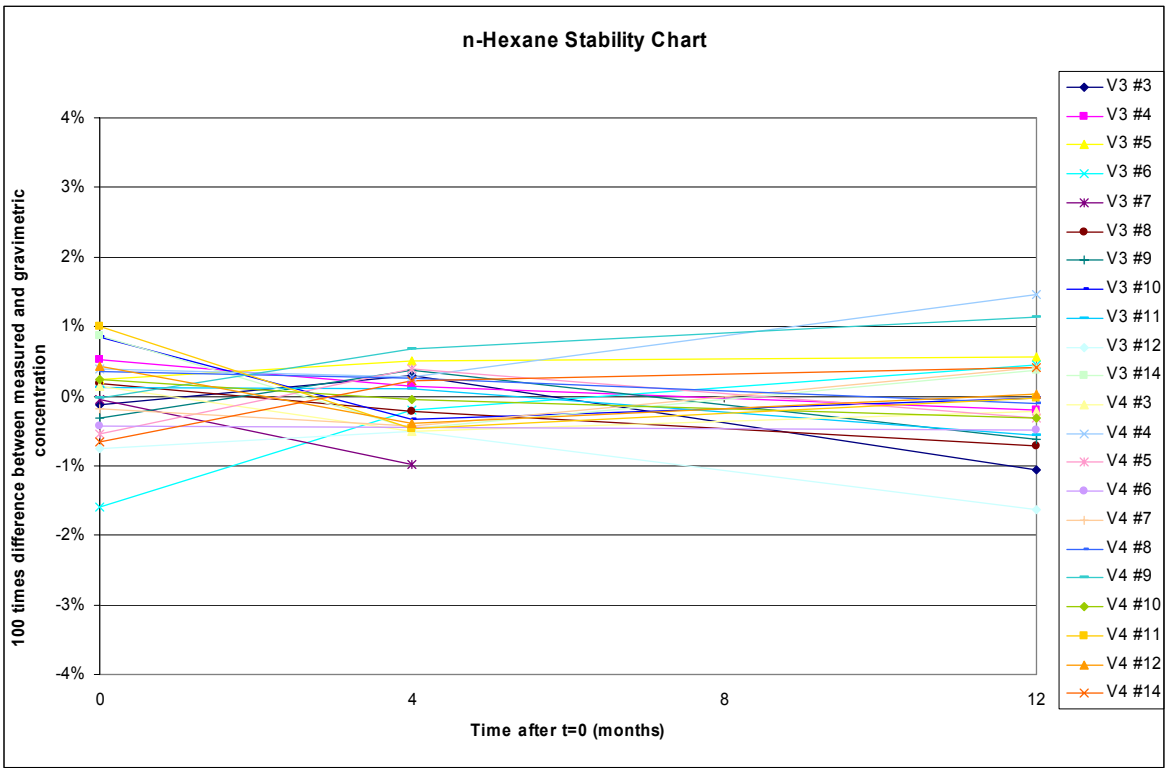
V4 #12
V4 #14


trans-2-Pentene Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


1-Pentene Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


2-methyl Pentane Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


n-Hexane Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
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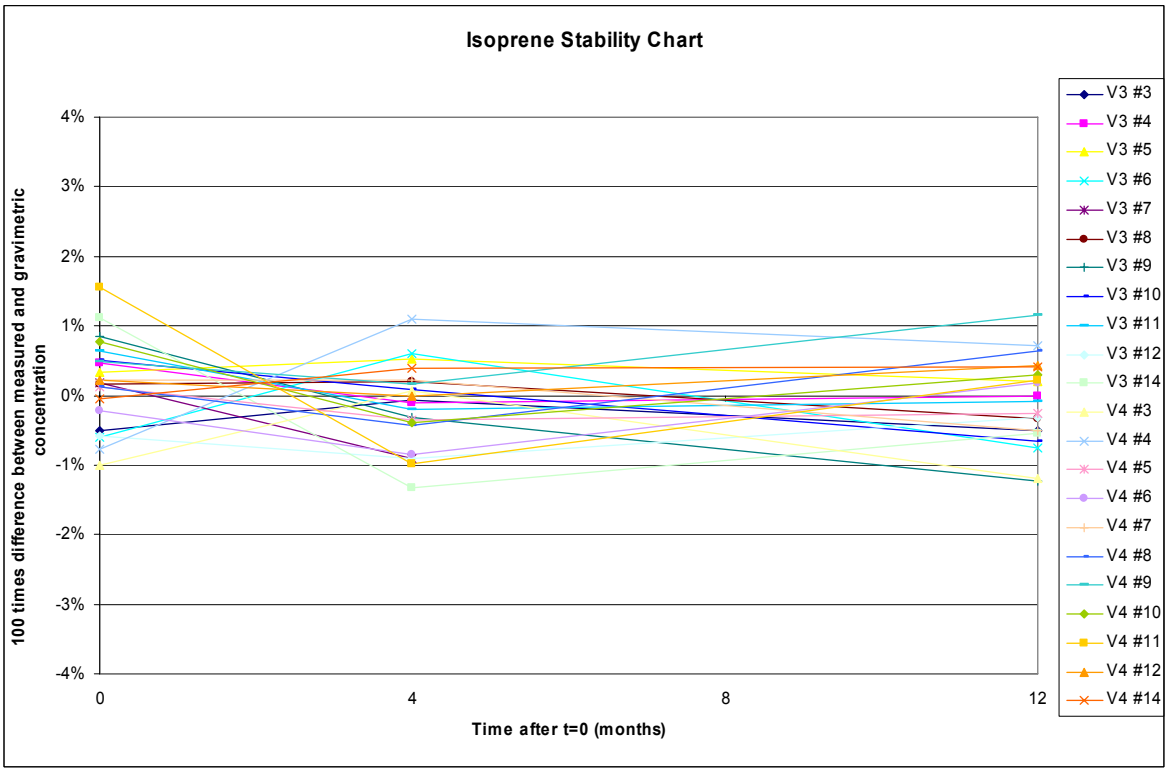
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


Isoprene Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
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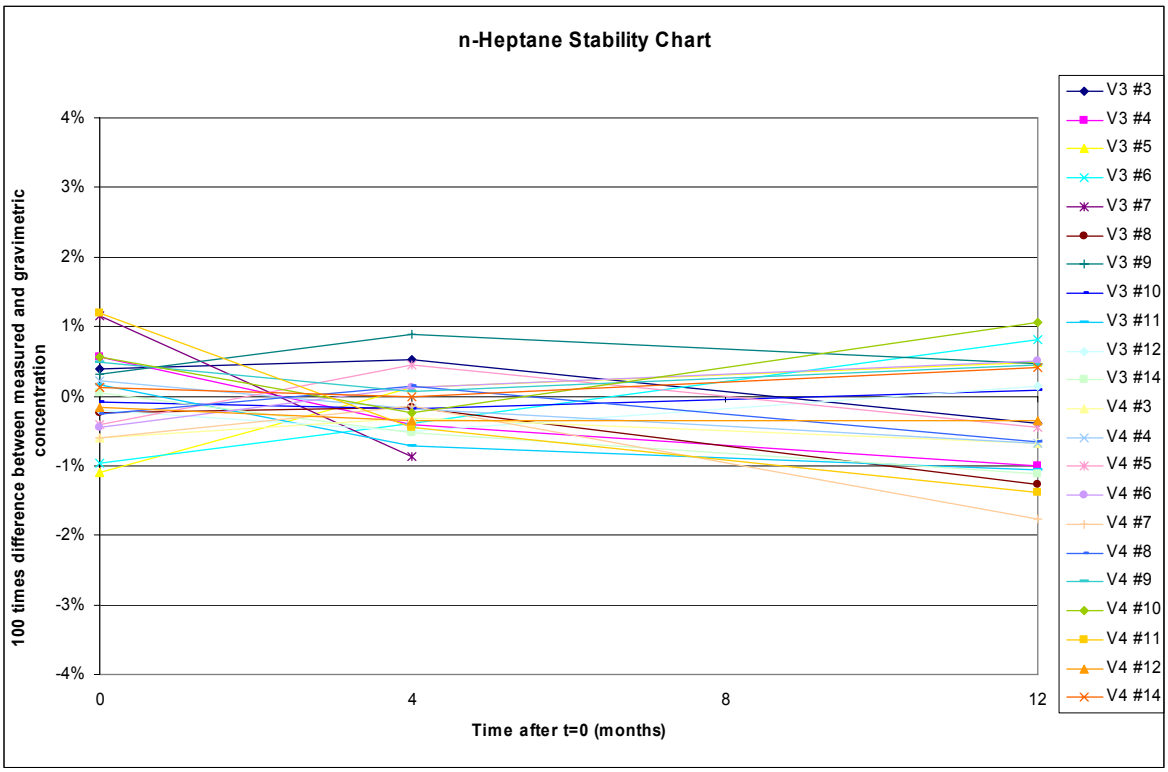
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


n-Heptane Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
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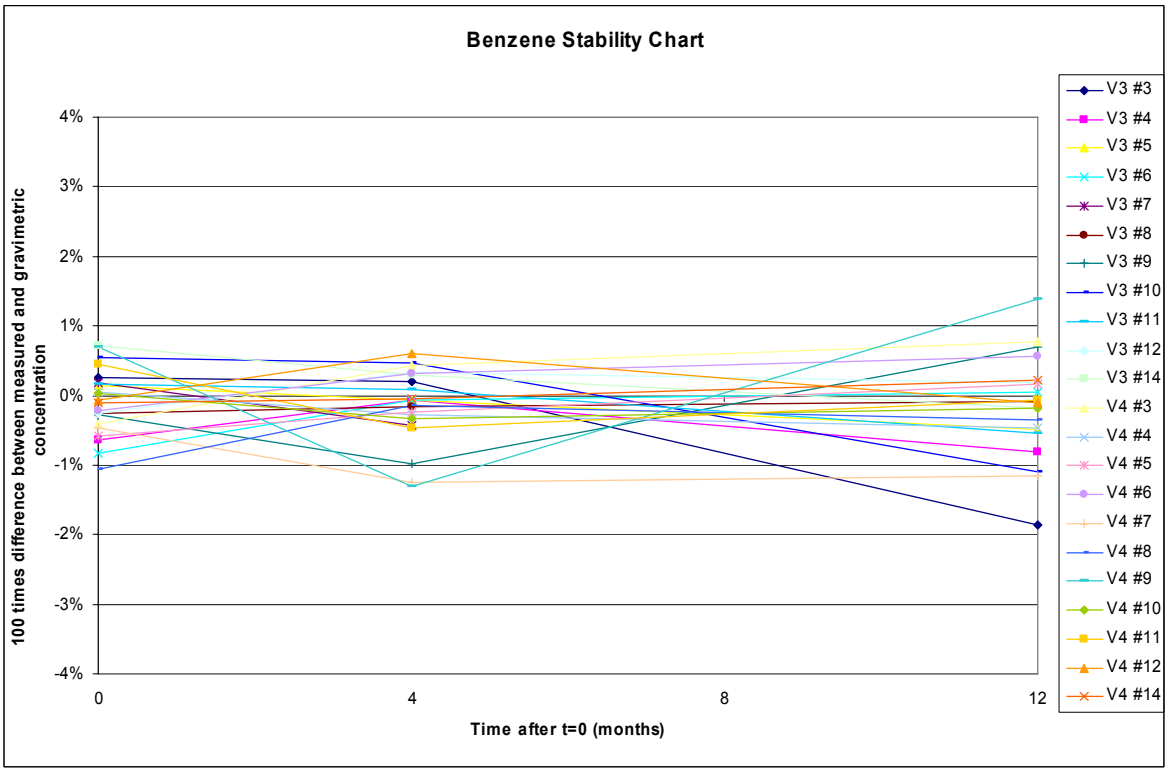
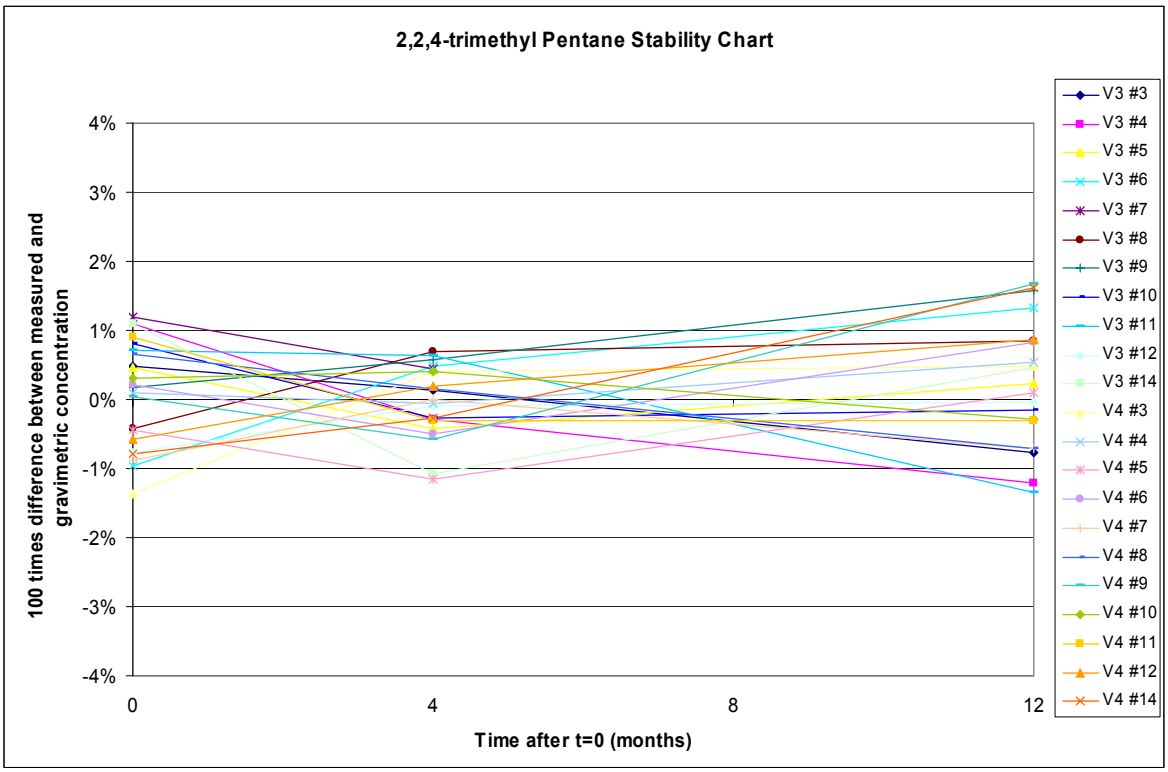
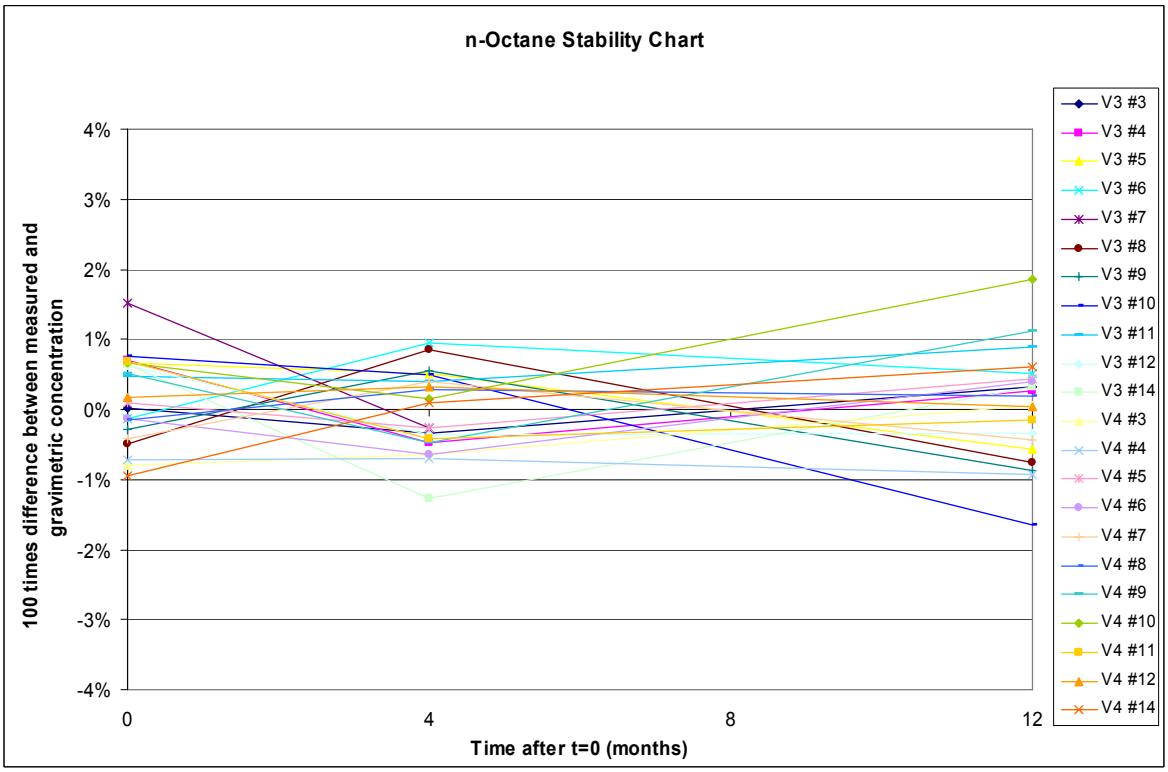
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


Benzene Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


2,2,4-trimethyl Pentane Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


n-Octane Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
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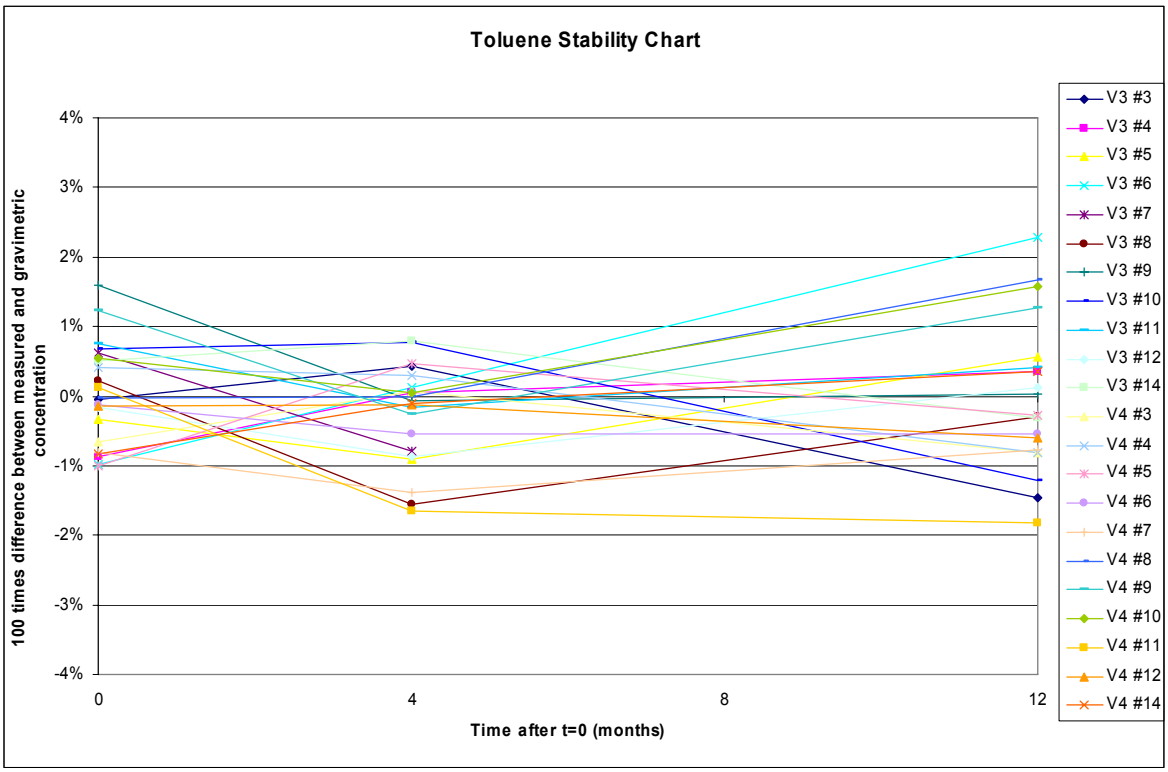
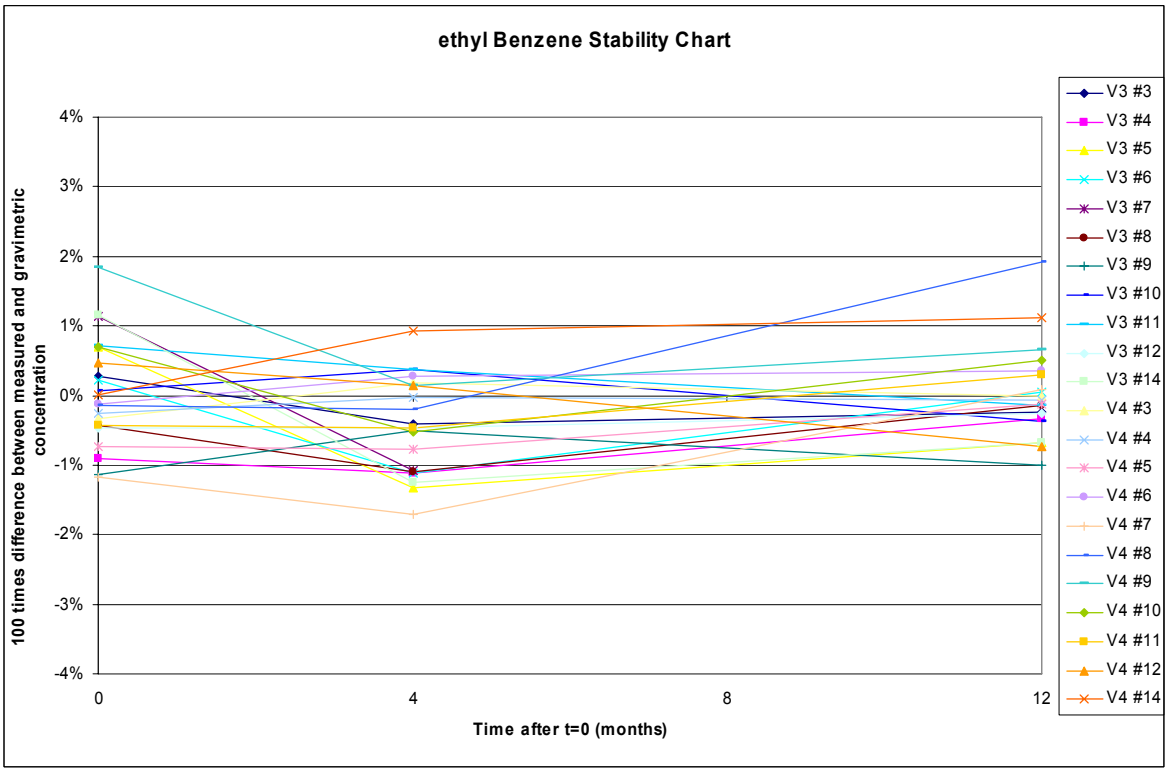
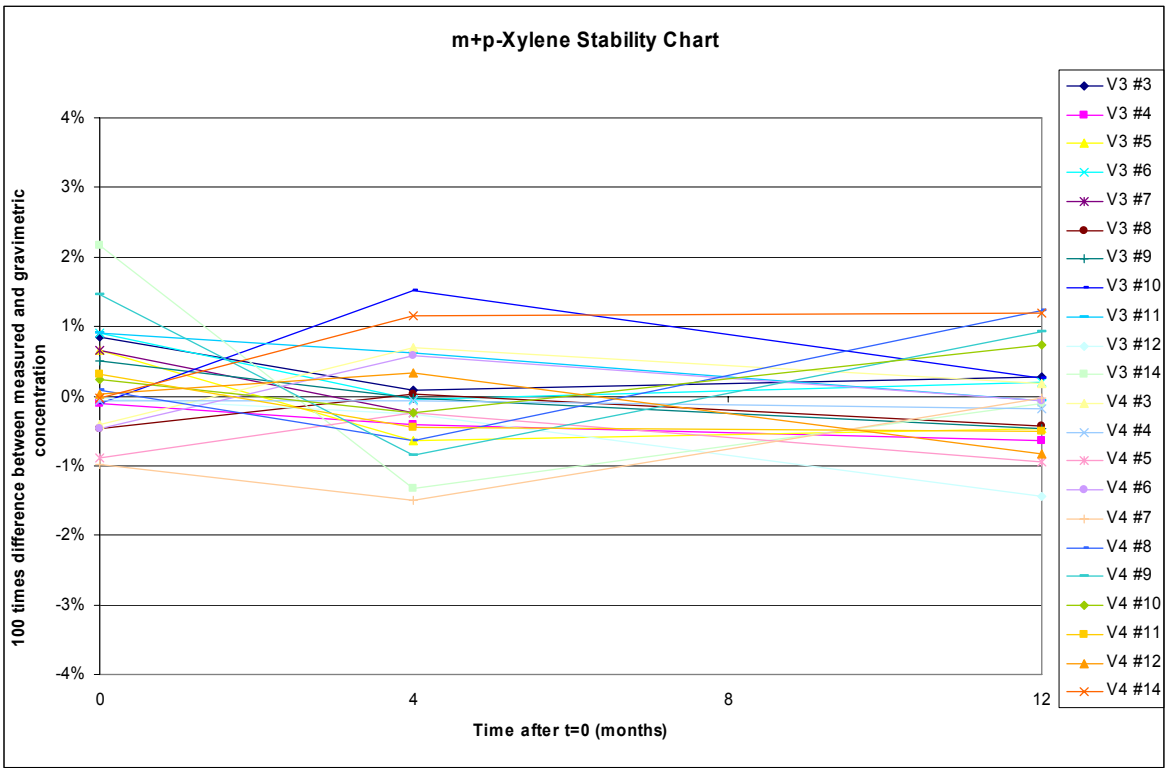
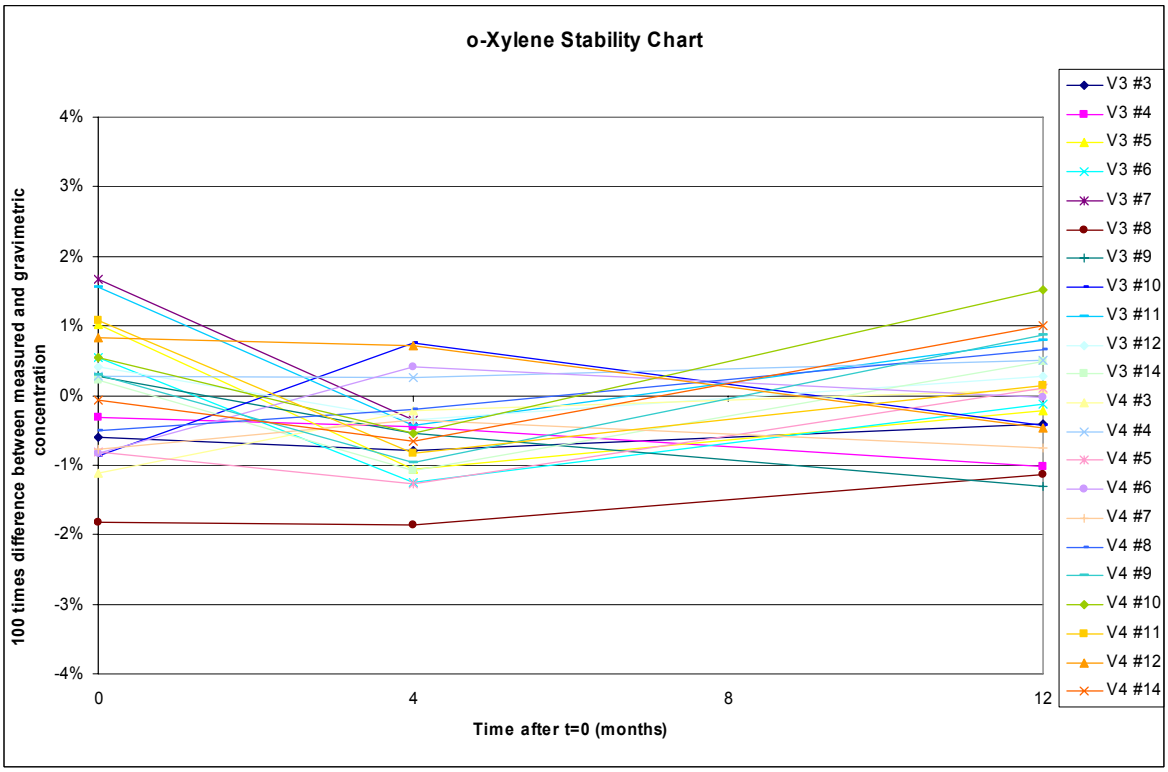
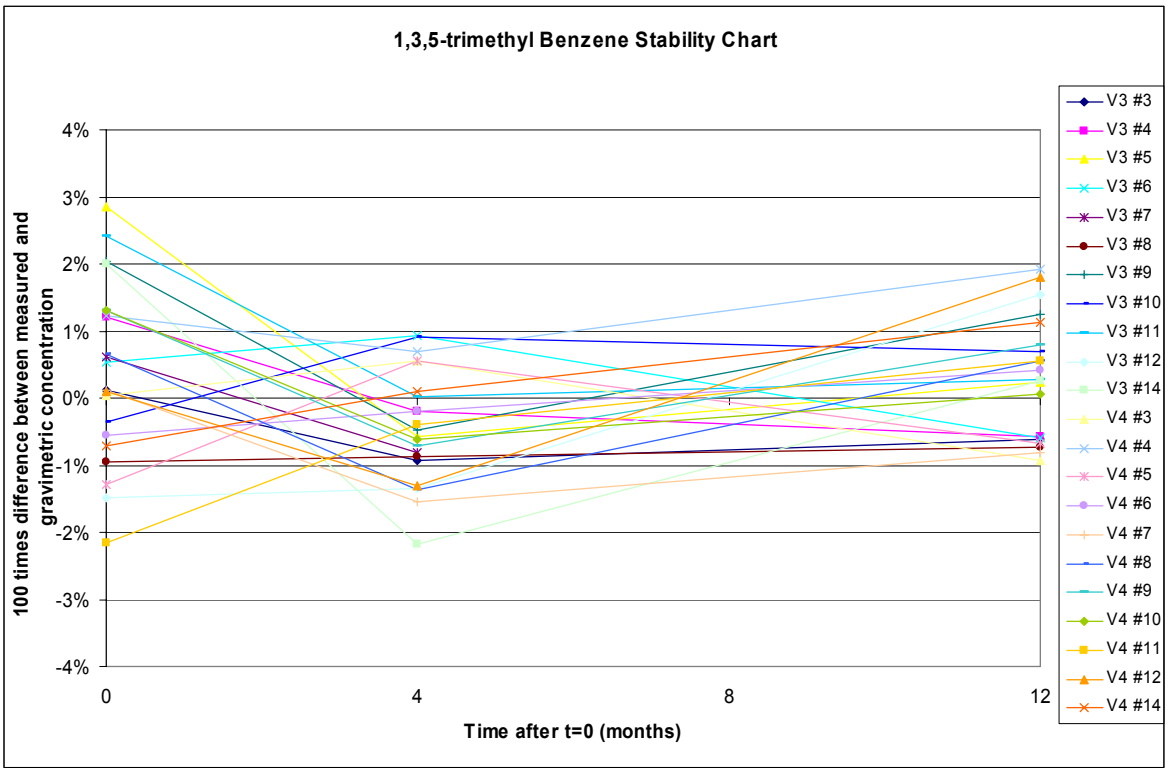
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

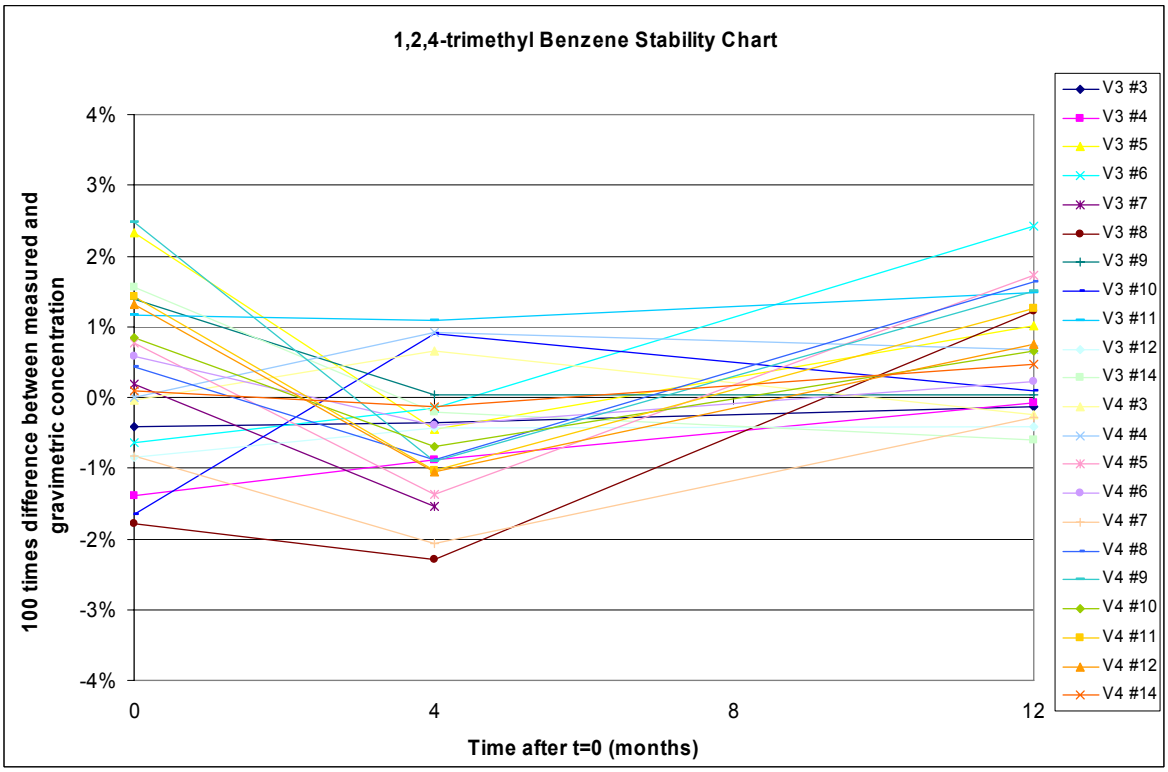

Toluene Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

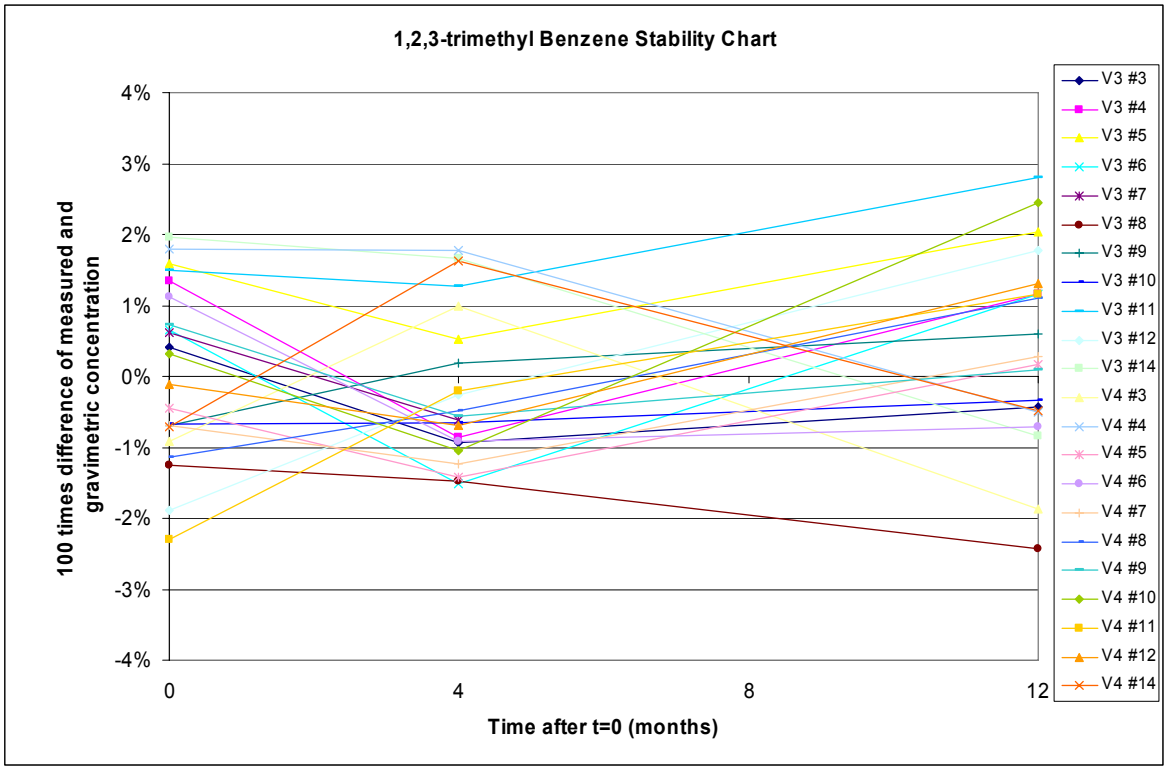

ethyl Benzene Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


m+p-Xylene Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


o-Xylene Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


1,3,5-trimethyl Benzene Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


1,2,4-trimethyl Benzene Stability Chart
100 times difference between measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14


1,2,3-trimethyl Benzene Stability Chart
100 times difference of measured and gravimetric concentration
4%
3%
2%
1%
0%
-1%
-2%
-3%
-4%
0
4
8
12
Time after t=0 (months)
V3 #3
V3 #4
V3 #5
V3 #6
V3 #7
V3 #8
V3 #9
V3 #10
V3 #11
V3 #12
V3 #14
V4 #3
V4 #4
V4 #5
V4 #6
V4 #7
V4 #8
V4 #9
V4 #10
V4 #11
V4 #12
V4 #14

Annex F: Supplementary Information

Table F1: Synthetic working standard amount fractions and associated gravimetric uncertainties.

Amount fraction (nmol/mol)										
	Version 3					Version 4				
Number:	#1	#2	#13	#15	U_g	#1	#2	#13	#15	U_g
ethane	6.74	6.74	6.74	6.74	0.02	5.91	5.92	5.92	5.92	0.02
ethene	6.70	6.69	6.69	6.69	0.02	5.87	5.87	5.88	5.88	0.02
propane	6.68	6.67	6.67	6.67	0.02	5.86	5.86	5.86	5.86	0.02
propene	6.60	6.59	6.60	6.59	0.02	5.78	5.79	5.79	5.79	0.02
iso-butane	7.11	7.10	7.10	7.10	0.01	7.97	7.97	7.97	7.97	0.01
n-butane	6.90	6.89	6.90	6.89	0.01	7.73	7.74	7.74	7.74	0.01
acetylene	6.68	6.68	6.68	6.68	0.02	5.86	5.86	5.86	5.86	0.02
trans-2-butene	6.90	6.89	6.89	6.89	0.01	7.73	7.73	7.74	7.73	0.01
1-butene	6.79	6.78	6.79	6.78	0.01	7.61	7.61	7.61	7.61	0.01
cis-2-butene	6.80	6.79	6.80	6.80	0.01	7.62	7.63	7.63	7.63	0.01
2-methyl butane	5.13	5.12	5.12	5.12	0.01	5.29	5.29	5.29	5.29	0.01
n-pentane	5.20	5.20	5.20	5.20	0.01	5.37	5.37	5.37	5.37	0.01
1,3-butadiene	6.60	6.59	6.59	6.59	0.02	5.78	5.78	5.79	5.79	0.01
trans-2-pentene	4.95	4.95	4.95	4.95	0.01	5.11	5.11	5.11	5.11	0.01
1-pentene	5.04	5.04	5.04	5.04	0.01	5.20	5.21	5.21	5.21	0.01
2-methyl pentane	5.13	5.13	5.13	5.13	0.01	5.29	5.30	5.30	5.30	0.01
n-hexane	5.14	5.13	5.14	5.13	0.01	5.30	5.30	5.30	5.30	0.01
isoprene	5.14	5.13	5.14	5.14	0.01	5.30	5.30	5.31	5.31	0.01
n-heptane	5.07	5.07	5.07	5.07	0.01	5.23	5.24	5.24	5.24	0.01
benzene	4.18	4.17	4.18	4.18	0.01	3.78	3.78	3.78	3.78	0.01
2,2,4-trimethyl pentane	5.17	5.16	5.17	5.17	0.01	5.33	5.34	5.34	5.34	0.01
n-octane	5.12	5.11	5.12	5.12	0.01	5.28	5.28	5.29	5.29	0.01
toluene	3.59	3.59	3.59	3.59	0.01	3.25	3.25	3.25	3.25	0.01
ethyl-benzene	3.84	3.84	3.84	3.84	0.03	4.21	4.22	4.22	4.22	0.03
m+p-xylene	7.59	7.59	7.59	7.59	0.08	8.34	8.34	8.34	8.34	0.08
o-xylene	3.77	3.76	3.77	3.77	0.03	4.14	4.14	4.14	4.14	0.03
1,3,5-trimethyl benzene	3.68	3.68	3.68	3.68	0.02	4.04	4.04	4.04	4.04	0.03
1,2,4-trimethyl benzene	3.86	3.86	3.86	3.86	0.03	4.24	4.24	4.24	4.24	0.03
1,2,3-trimethyl benzene	3.52	3.51	3.52	3.52	0.03	3.86	3.86	3.86	3.86	0.03

U_g – expanded uncertainty (k=2) associated with gravimetric amount fraction

All working standards were verified using NPL primary standards to within the analytical uncertainty for each species stated in Annex D.

Working standards were prepared directly from high concentration parent mixtures to eliminate errors associated with drifts common to the reference and test cylinders.

The mother mixtures of the two versions (V3 and V4) were used to make 4 working standards each (#1, #2, #13 & #15). Working standards #1 & #2 were made and used in the stability trials at T = 0, working standards #13 were made and used at T = 4 months and working standards #15 were made and used at T = 12 months. Test cylinders were analysed against working standards from the opposing version to minimise errors associated with correlation.

Table F2: Synthetic standard mother mixture amount fractions and associated gravimetric uncertainties (nmol/mol).

Component	Mother V3 D95 4939	U_g	Mother V4 D95 4773	U_g
ethane	329.34	0.83	288.55	0.74
ethene	327.54	0.85	286.98	0.76
propane	326.06	0.76	285.70	0.68
propene	323.23	0.76	283.20	0.69
iso-butane	348.06	0.45	390.01	0.51
n-butane	337.88	0.46	378.60	0.51
acetylene	327.43	0.84	286.88	0.76
trans-2-butene	337.81	0.50	378.45	0.56
1-butene	332.52	0.48	372.44	0.53
cis-2-butene	333.10	0.50	373.17	0.56
2-methyl butane	251.08	0.44	258.95	0.45
n-pentane	254.72	0.44	262.71	0.46
1,3-butadiene	323.06	0.71	283.09	0.64
trans-2-pentene	242.54	0.53	250.15	0.55
1-pentene	247.05	0.34	254.80	0.35
2-methyl pentane	251.31	0.34	259.19	0.35
n-hexane	251.62	0.38	259.51	0.39
isoprene	251.70	0.46	259.59	0.47
n-heptane	248.42	0.35	256.22	0.37
benzene	204.64	0.28	184.93	0.26
2,2,4-trimethyl pentane	253.20	0.33	261.15	0.34
n-octane	250.77	0.34	258.64	0.36
toluene	175.96	0.24	159.02	0.23
ethyl-benzene	188.03	1.32	206.30	1.45
m+p-xylene	371.95	1.87	408.09	2.05
o-xylene	184.57	1.31	202.50	1.44
1,3,5-trimethyl benzene	180.30	1.17	197.81	1.29
1,2,4-trimethyl benzene	189.07	1.22	207.44	1.34
1,2,3-trimethyl benzene	172.30	1.43	189.04	1.57

U_g – expanded uncertainty (k=2) associated with gravimetric amount fraction

The mother mixtures were verified against each other at the start of the exercise (T=0). Stability checks were made on the mother mixtures indirectly as they were diluted to produce low concentration working standards for the stability tests at T = 4 and 12 months, which were themselves verified. From these and NPL's experience with similar mixtures, the best estimates for concentration and uncertainty at T = 4 and T = 12 months are the same as those at T = 0.

Table F3: Relative uncertainties associated with the reported amount fractions of synthetic test cylinders.

	u_{prec}	u_{ref}	Combined uncertainty (k=1)	Expanded uncertainty(k=2)
ethane	0.68%	0.16%	0.70%	**1.40%**
ethene	0.51%	0.15%	0.53%	**1.06%**
propane	0.65%	0.15%	0.67%	**1.33%**
propene	1.02%	0.13%	1.03%	**2.06%**
iso-butane	1.11%	0.09%	1.11%	**2.23%**
n-butane	0.77%	0.09%	0.78%	**1.55%**
acetylene	0.87%	0.14%	0.88%	**1.76%**
trans-2-butene	0.50%	0.10%	0.51%	**1.02%**
1-butene	0.67%	0.09%	0.68%	**1.35%**
cis-2-butene	0.83%	0.10%	0.84%	**1.67%**
2-methyl butane	0.75%	0.11%	0.76%	**1.51%**
n-pentane	0.76%	0.10%	0.77%	**1.53%**
1,3-butadiene	0.62%	0.12%	0.63%	**1.26%**
trans-2-pentene	0.65%	0.13%	0.66%	**1.32%**
1-pentene	0.70%	0.09%	0.71%	**1.41%**
2-methyl pentane	0.77%	0.09%	0.78%	**1.55%**
n-hexane	0.58%	0.10%	0.59%	**1.18%**
isoprene	0.59%	0.11%	0.60%	**1.20%**
n-heptane	0.64%	0.09%	0.65%	**1.29%**
benzene	0.57%	0.09%	0.58%	**1.15%**
2,2,4-trimethyl pentane	0.74%	0.09%	0.75%	**1.49%**
n-octane	0.64%	0.09%	0.65%	**1.29%**
toluene	0.86%	0.09%	0.86%	**1.73%**
ethyl-benzene	0.67%	0.36%	0.76%	**1.52%**
m+p-xylene	0.70%	0.51%	0.87%	**1.73%**
o-xylene	0.76%	0.36%	0.84%	**1.68%**
1,3,5-trimethyl benzene	1.03%	0.33%	1.08%	**2.16%**
1,2,4-trimethyl benzene	1.00%	0.33%	1.05%	**2.11%**
1,2,3-trimethyl benzene	1.24%	0.42%	1.31%	**2.62%**

u_{ref} is the uncertainty due to reference working standard

The associated uncertainty of a single measurement was calculated by combining in quadrature (as k=1) the analytical uncertainty given by the precision of measurements over the 3 rounds of analysis (u_{prec}) and the gravimetric uncertainty associated with the reference cylinder (u_{ref}). These were then converted to expanded uncertainties at a 95% confidence level. The uncertainties apply to the measurements at T = 0, 4 and 12 months.

Annex D explains the calculation of u_{prec} in both the synthetic and ambient cases.

Table F4: Relative uncertainties associated with all reported amount fractions of the ambient test cylinders including those of the ambient mother stock before and after decant.

	u_{prec}	U_l (k=2)	U_{ref} (k=2)	Combined uncertainty (k=1)	**Expanded uncertainty(k=2)**
ethane	0.77%	1.0%	1.0%	1.05%	**2.09%**
ethene	2.06%	1.0%	1.0%	2.18%	**4.36%**
propane	1.50%	1.0%	1.0%	1.66%	**3.32%**
propene	2.46%	1.0%	1.0%	2.56%	**5.12%**
iso-butane	2.91%	1.5%	1.0%	3.05%	**6.09%**
n-butane	0.99%	1.0%	1.0%	1.22%	**2.43%**
acetylene	2.37%	1.0%	1.5%	2.54%	**5.07%**
trans-2-butene	2.32%	1.0%	1.0%	2.43%	**4.85%**
1-butene	1.96%	1.0%	1.0%	2.08%	**4.17%**
i-butene	2.59%	1.5%	1.5%	2.80%	**5.60%**
cis-2-butene	2.16%	1.0%	1.0%	2.27%	**4.55%**
2-methyl butane	1.06%	1.0%	1.0%	1.27%	**2.55%**
n-pentane	2.47%	1.0%	1.0%	2.57%	**5.14%**
propyne	3.39%	1.5%	1.5%	3.55%	**7.10%**
1,3-butadiene	2.07%	1.5%	1.0%	2.26%	**4.52%**
trans-2-pentene	1.15%	1.0%	1.0%	1.35%	**2.70%**
1-pentene	3.29%	1.5%	1.0%	3.41%	**6.82%**
cis-pentene	2.18%	1.5%	1.5%	2.42%	**4.85%**
cyclohexane	2.41%	2.0%	1.5%	2.71%	**5.43%**
2-methyl pentane	2.74%	2.0%	1.5%	3.01%	**6.02%**
3-methyl pentane	3.50%	2.0%	2.0%	3.77%	**7.55%**
n-hexane	1.54%	1.0%	1.0%	1.69%	**3.39%**
isoprene	2.68%	2.0%	1.5%	2.96%	**5.91%**
n-heptane	1.68%	2.0%	1.0%	2.02%	**4.04%**
benzene	2.28%	1.5%	1.0%	2.45%	**4.90%**
2,2,4-trimethyl pentane	2.97%	2.0%	1.0%	3.17%	**6.35%**
n-octane	4.22%	2.0%	1.0%	4.37%	**8.73%**
toluene	1.03%	2.0%	1.5%	1.62%	**3.24%**
ethyl-benzene	2.56%	3.0%	1.5%	3.06%	**6.12%**
m+p-xylene	2.08%	3.0%	1.5%	2.67%	**5.34%**
o-xylene	2.01%	3.0%	1.5%	2.62%	**5.24%**
1,3,5-trimethyl benzene	3.62%	3.5%	2.0%	4.14%	**8.29%**
1,2,4-trimethyl benzene	4.64%	3.5%	2.0%	5.06%	**10.12%**
1,2,3-trimethyl benzene	4.90%	3.5%	2.0%	5.30%	**10.60%**

U_l – uncertainty due to linearity and chromatographic error

U_{ref} – uncertainty due to the reference standard. These values are larger than for the specially prepared reference standards used for the synthetic mixtures because the ambient mixtures were labelled independently using our routine procedures. The associated uncertainty of a single measurement was calculated by combining in quadrature (as k=1) the analytical uncertainty given by the precision of measurements over the 2 rounds of analysis, the gravimetric uncertainty associated with the reference cylinder and the uncertainty due to linearity and chromatographic error.

Table F5: Indicative VOC amount fractions of the Bushy Park, Teddington air used to dilute the ambient mother mixture

Component	Amount fraction (nmol/mol)	
	Compressed air sample (Teddington)	Expanded uncertainty (k=2)
ethane	1.93	0.06
ethene	0.39	0.04
propane	0.58	0.04
propene	0.16	0.04
iso-butane	0.31	0.04
n-butane	0.57	0.04
acetylene	0.28	0.04
trans-2-butene	0.00	0.04
1-butene	0.00	0.04
i-butene	0.00	0.04
cis-2-butene	0.00	0.04
2-methyl butane	0.39	0.04
n-pentane	0.15	0.04
propyne	0.00	0.04
1,3-butadiene	0.00	0.04
trans-2-pentene	0.00	0.04
1-pentene	0.02	0.04
cis-pentene	0.00	0.04
cyclohexane	0.00	0.04
2-methyl pentane	0.00	0.04
3-methyl pentane	0.00	0.04
n-hexane	0.06	0.04
isoprene	0.08	0.04
n-heptane	0.05	0.04
benzene	0.12	0.04
2,2,4-trimethyl pentane	0.00	0.04
n-octane	0.05	0.04
toluene	0.26	0.04
ethyl-benzene	0.09	0.04
m+p-xylene	0.22	0.04
o-xylene	0.13	0.04
1,3,5-trimethyl benzene	0.36	0.04
1,2,4-trimethyl benzene	0.48	0.04
1,2,3-trimethyl benzene	0.47	0.04

Because of the method and equipment used to prepare the ambient mother mixture, the Teddington air that forms 99% of this mixture could not be analysed directly. Table F5 is an analysis of Teddington air taken during the validation of the method. It is therefore not expected to have exactly the same composition as the air sampled at the time the ambient mother mixture were prepared. However, it gives a good indication of the VOC components present in the real air used.

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Abstract

Between May 2007 and February 2008, cylinders from two mixtures (synthetic and ambient air) circulated amongst 18 AQUILA laboratories to evaluate their performance in the analysis of the 30 volatile organic compounds listed in the directive EC/50/2008.

The concentration for the compared mixtures was of circa 5 and 1 ppb per compound in the synthetic and ambient air mixture, respectively. Laboratories were asked to carry out five independent measurements for each mixture and provide values and associated uncertainties. A full description of the analytical method used by each laboratory and their calculations for the estimation of the uncertainties was also included in the report.

The results were finally expressed in terms of bias with respect to the reference value and the E_n number of the measurement. In general, analytical uncertainties were higher for the lower concentration mixture in comparison to the higher one. For the synthetic mixture, half of the laboratories reported relative overall expanded uncertainties better than 10 %, whilst for the ambient air mixture, the same percentage of laboratories showed only values better than 20 %.

The heaviest hydrocarbons (123, 124 and 135 trimethyl benzene, m,p- xylene, ethyl-benzene and benzene) and those more reactive and lighter (like 1,3 butadiene, isoprene, 1-pentene) were analysed with more difficulty in comparison to the rest of the compounds.

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